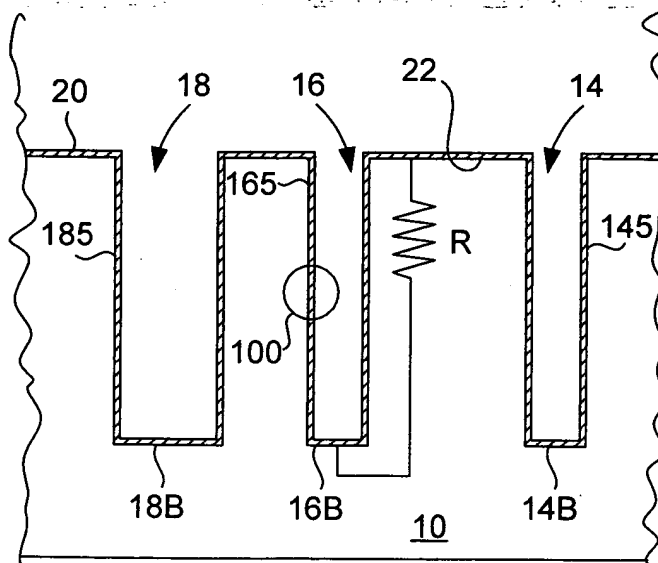
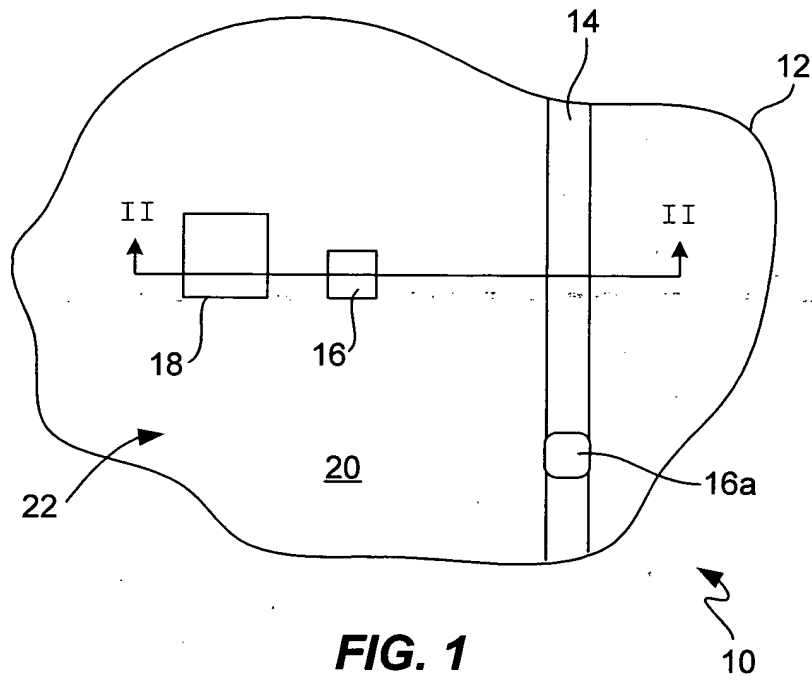




Best Available Copy



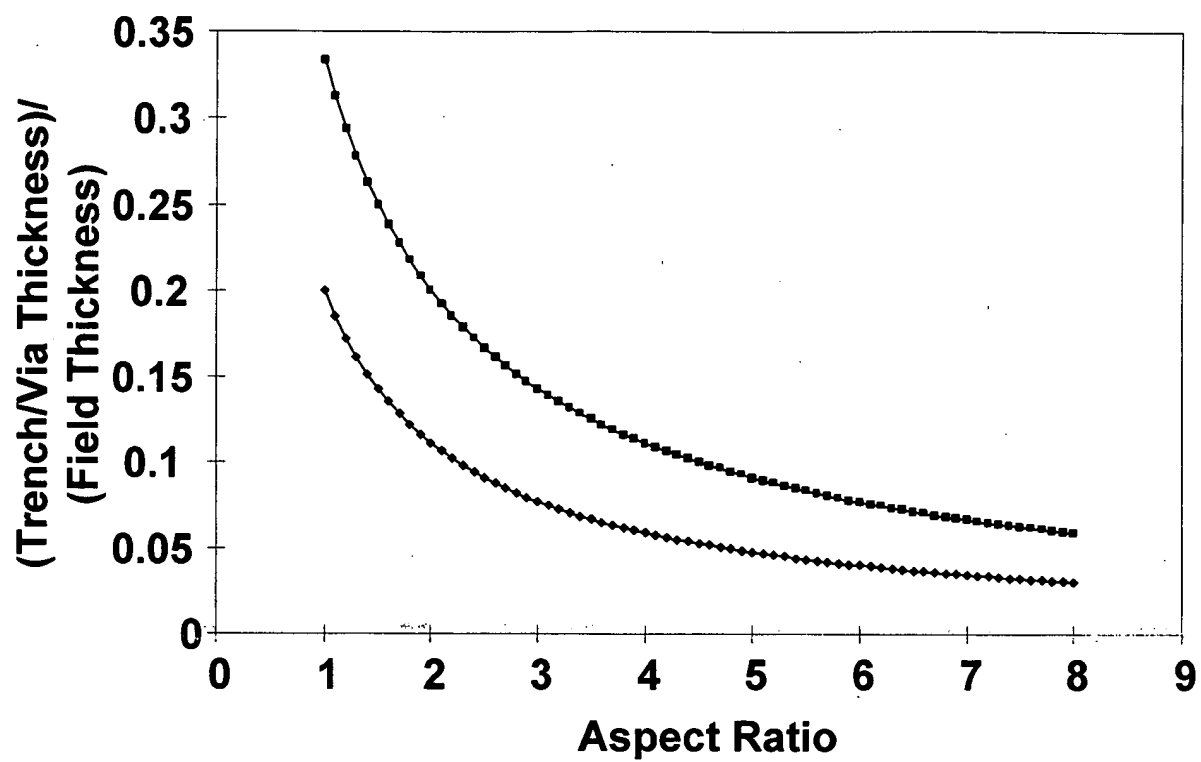


FIG. 3

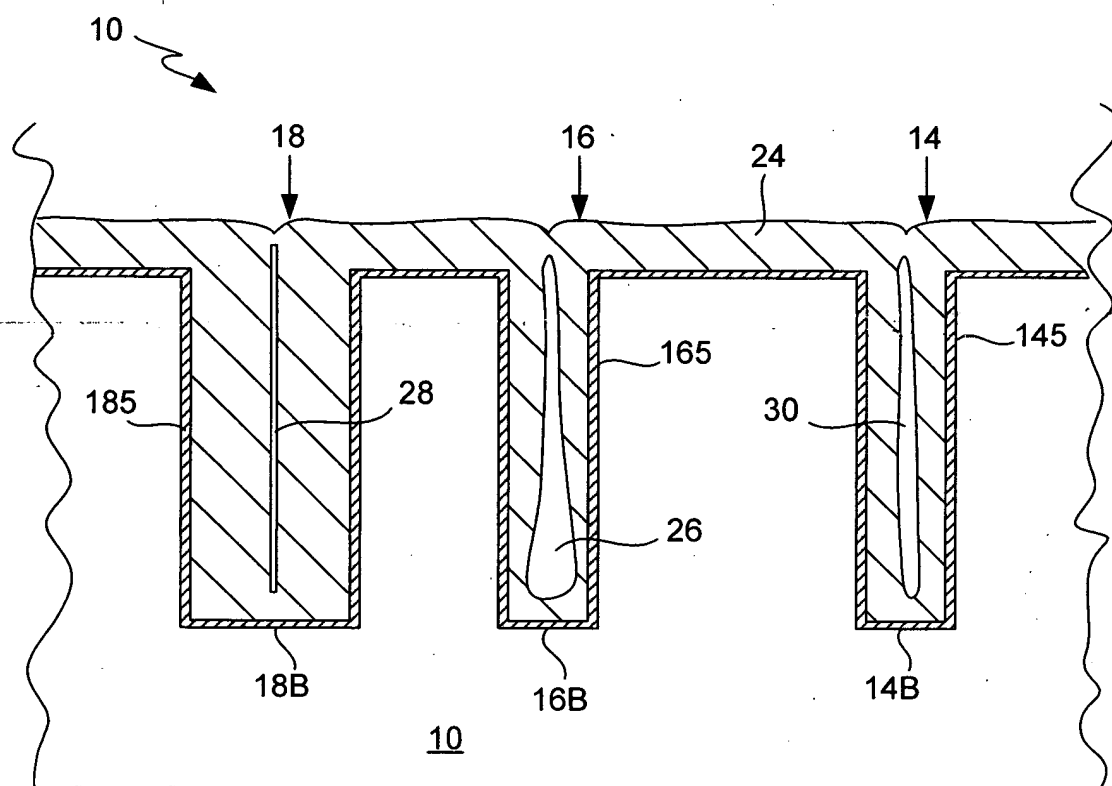


FIG. 4

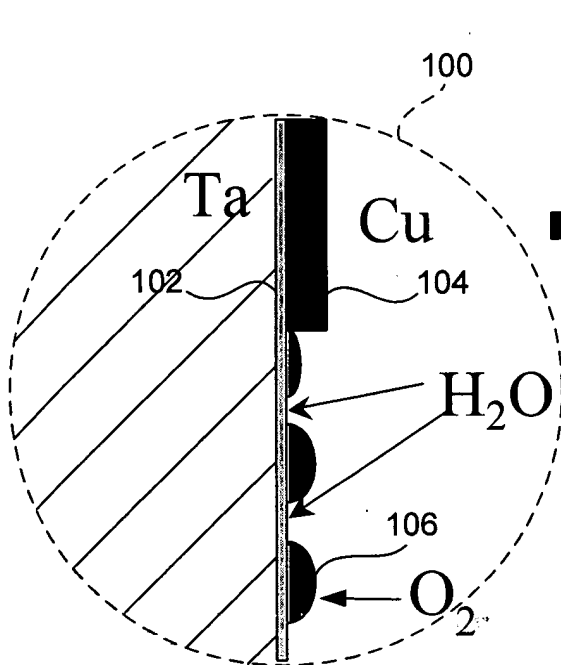


FIG. 5A

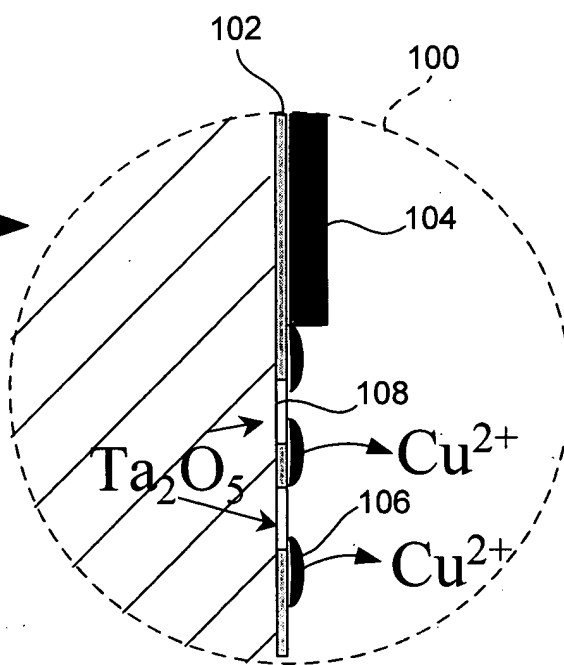


FIG. 5B

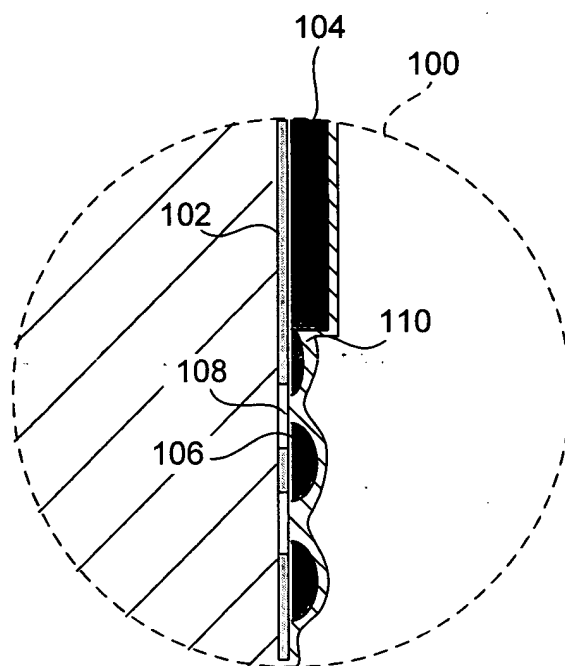


FIG. 6

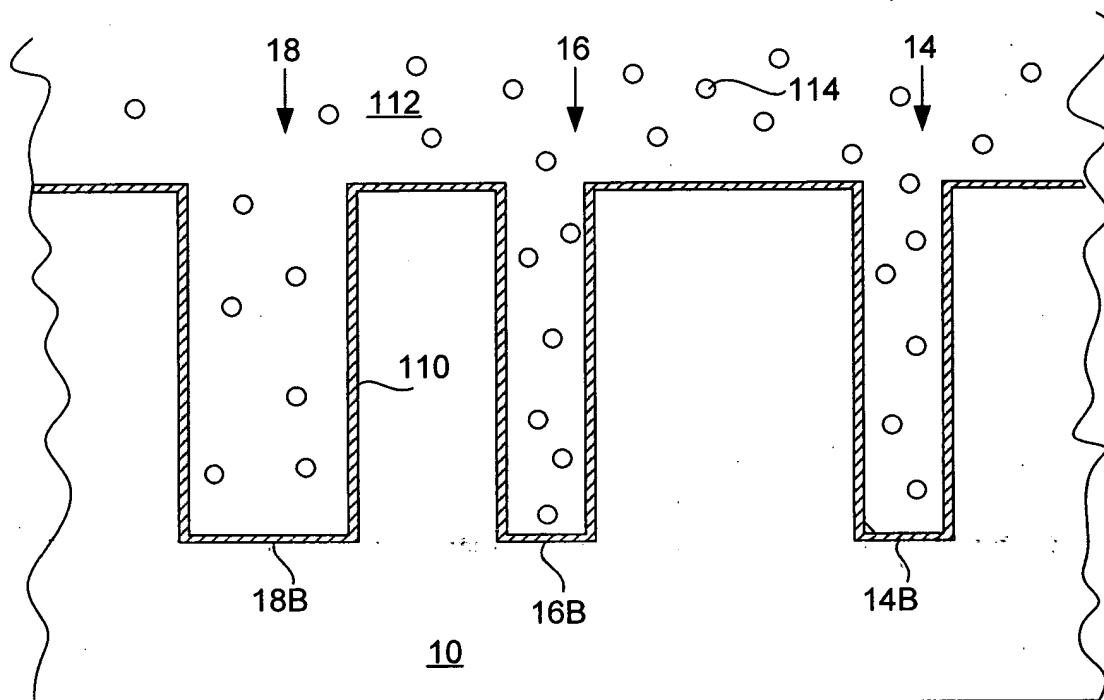


FIG. 7

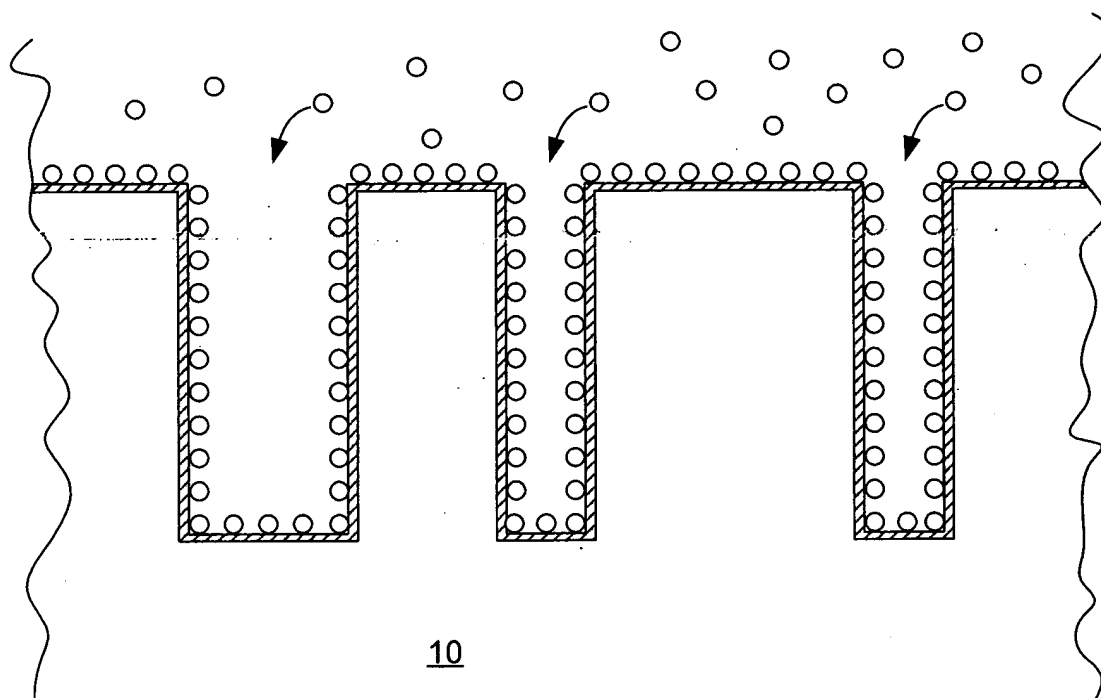


FIG. 8

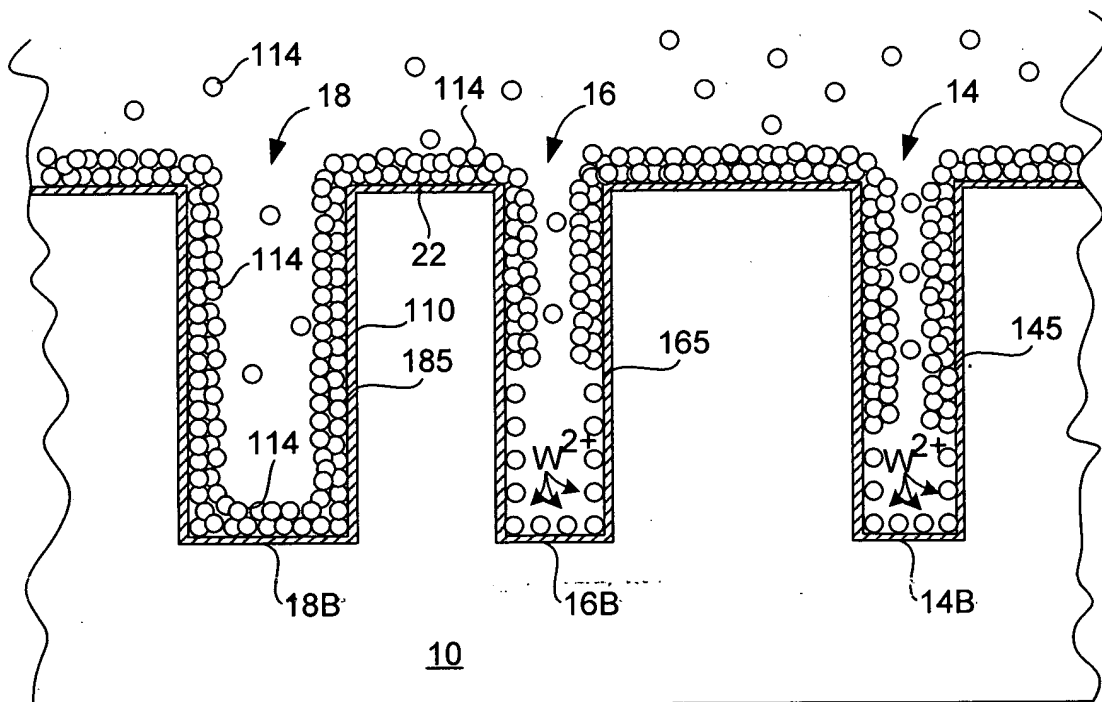
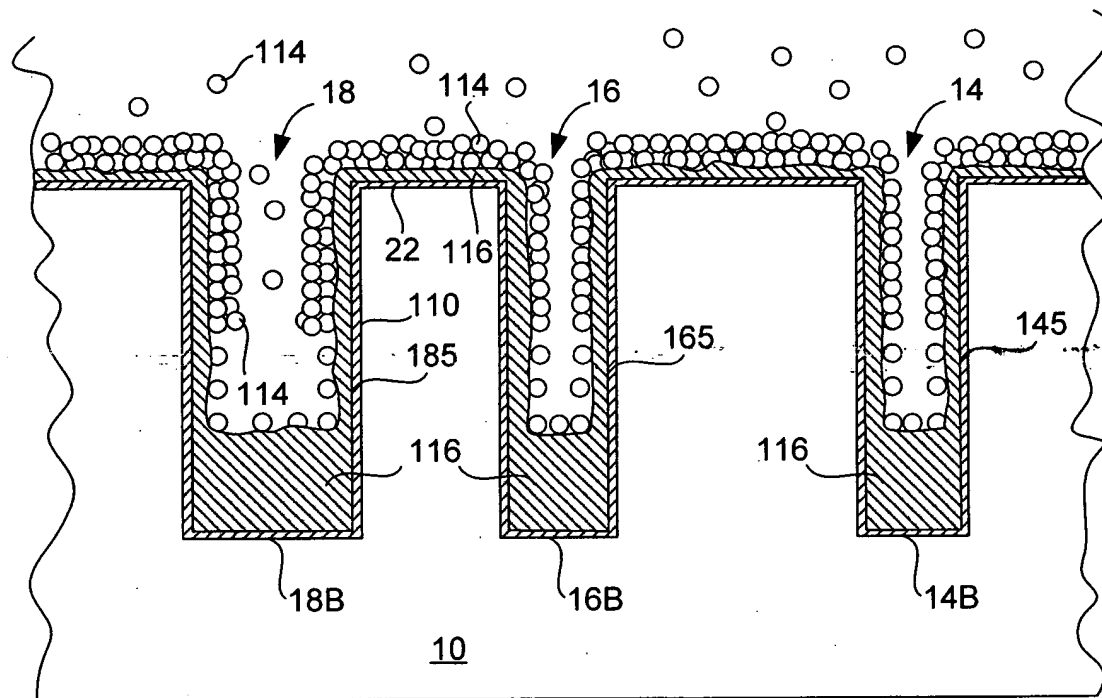


FIG. 9

**FIG. 10**

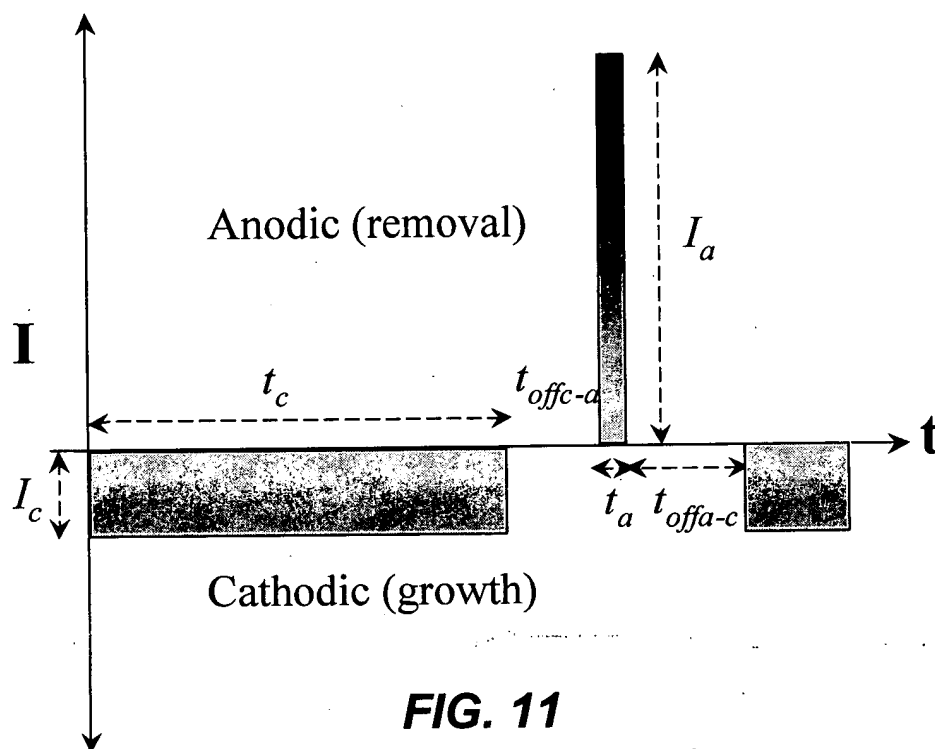


FIG. 11

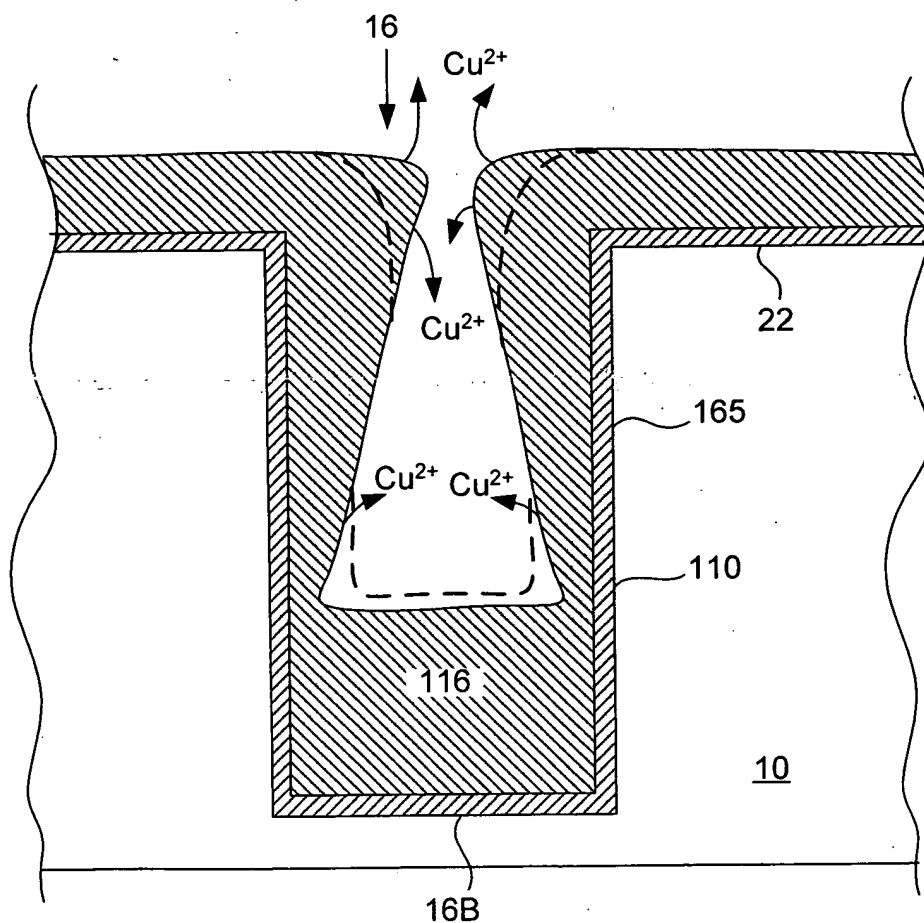


FIG. 12

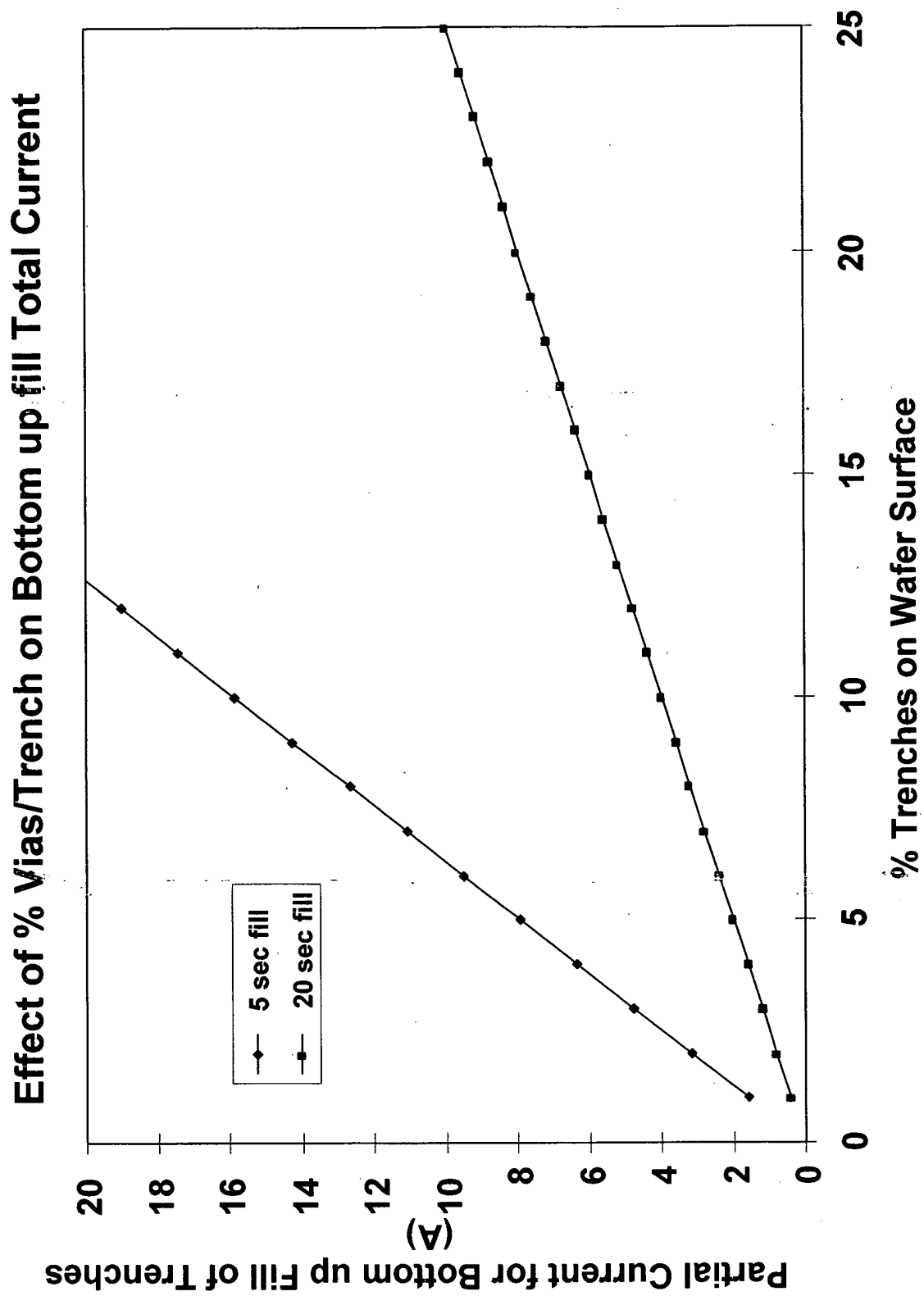
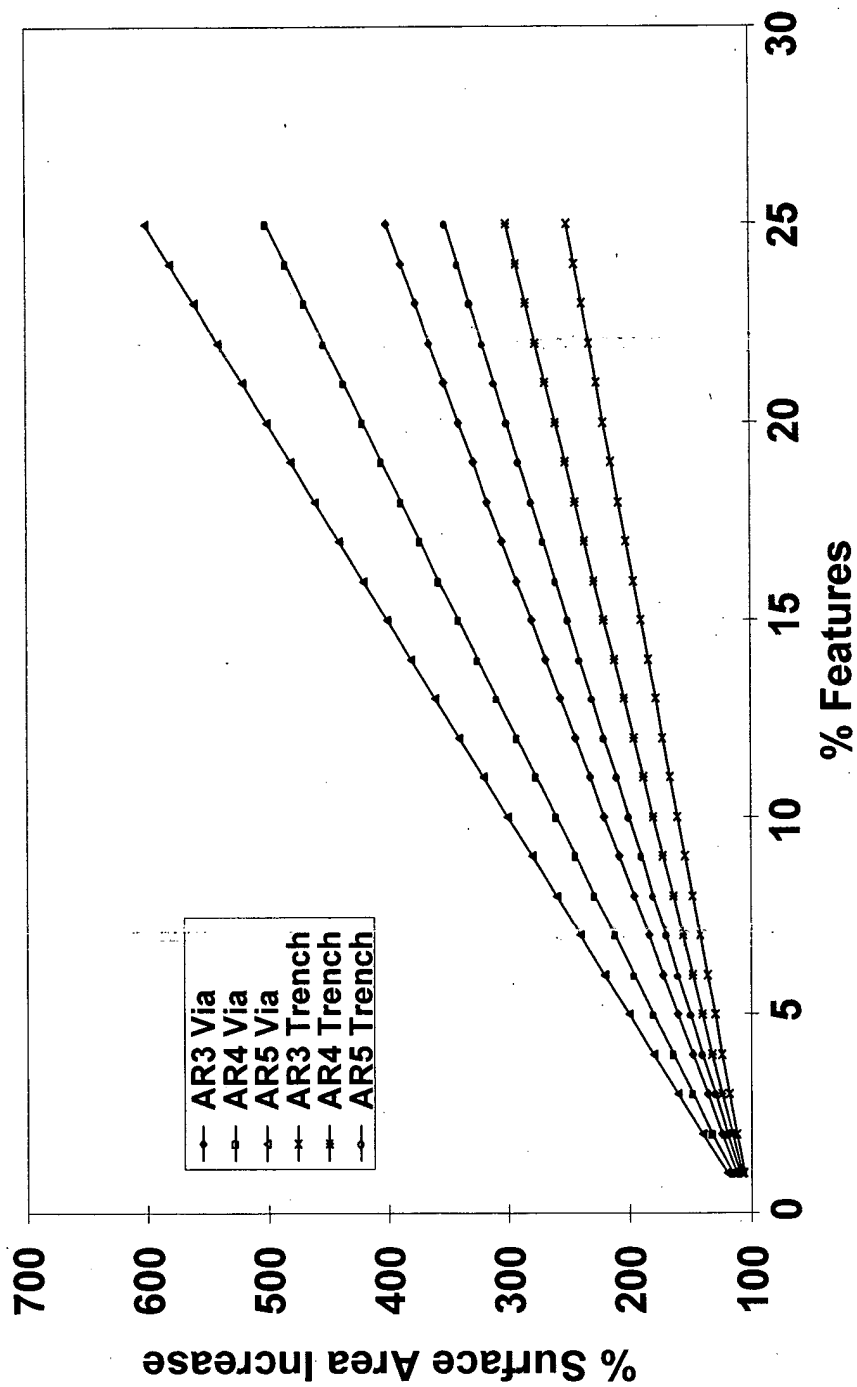


FIG. 13

Surface Area with Features of various Aspect Ratios



$$\frac{A_{total}}{A_{wafer}} = f_{field} + \sum_{i=1}^n f_i [1 + 4A] + \sum_{j=1}^m f_j [1 + 2A]$$

FIG. 14

How Much Additive Comes in With the Solution?

Ratio:

Surface to Solution Molecules

Aspect Ratio	2	2.5	3	3.5	4	4.5	5	5.5
	299	365	432	498	565	631	697	764
	60	73	86	100	113	126	139	153
	155	190	224	259	293	327	362	396
	52	63	75	86	98	109	121	132

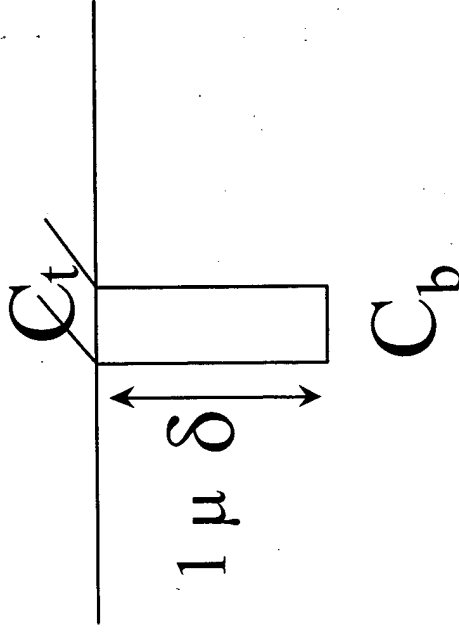
Conditions	ppm	20	100	100	100	300
MW		100	100	100	3000	3000
Moles/um^3		2.0E-19	1.0E-18	3.3E-20	1E-19	1E-19
Molec/um^3		120460	602300	20077	60230	60230
Molecules size (nm)		0.5	0.5	1.7	1.7	1.7
Molec/um^2		4000000	4000000	346021	346020.8	346020.8

Conclusion: At all expected additive condition, there is insufficient material stored in the initial solution within the via to lead to substantial surface absorption in the via.
 -There will be an absorption time delay.

FIG. 15

Time Estimate for Plating Additives Absorption

Assumptions



1. Initial surface coverage is zero
2. Final surface coverage is 1×10^{15} molecules/cm² (1 monolayer).
3. Very fast absorption kinetics (diffusion controlled)
4. No side wall absorption

Conclusions

1. Diffusion controlled absorption inside of trench take a few seconds.
2. Larger surface area of trench will increase this time from this estimate.
3. High additive level will decrease time estimate

$$\Delta C = 10\text{ ppm} = 5.5 \times 10^{-8}\text{ M} / \text{cm}^3$$

$$\delta = 1\ \mu = 1.0 \times 10^{-4}\text{ cm}$$

$$D = 1.0 \times 10^{-6}\text{ cm}^2 / \text{sec}$$

$$F = \frac{D\Delta C}{\delta} = 5 \times 10^{-10}\text{ M} / \text{sec cm}^2 = 3.4 \times 10^{14}\text{ molecules} / \text{sec cm}^2$$

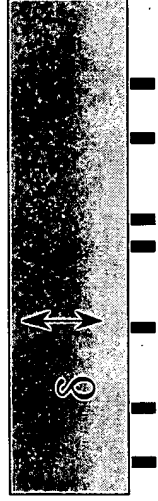
$$t_{\text{abs}} = 1 \times 10^{-15}\text{ molecules} / \text{cm}^2 / 3.4 \times 10^{14}\text{ molecules} / \text{sec cm}^2 = 2.9\text{ sec}$$

FIG. 16

Time Estimate for Absorption of Plating Additives

Assumptions

1. Initial surface coverage is zero everywhere
2. Final surface coverage is 1×10^{15} molecules/cm² (1 monolayer).
3. Very fast absorption kinetics (diffusion controlled)
4. Concentration at edge of boundary layer is bulk



Conclusions

Diffusion of very low concentration plating additives may take several seconds to occur

$$\Delta C = 10 \text{ ppm} = 5.5 \times 10^{-8} \text{ M} / \text{cm}^3$$

$$\delta = 5.7 \mu = 5.7 \times 10^{-4} \text{ cm}$$

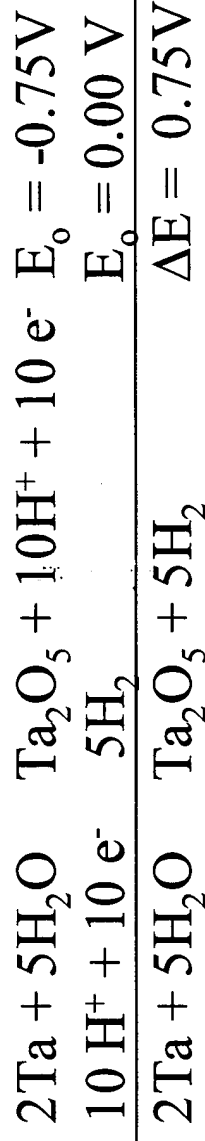
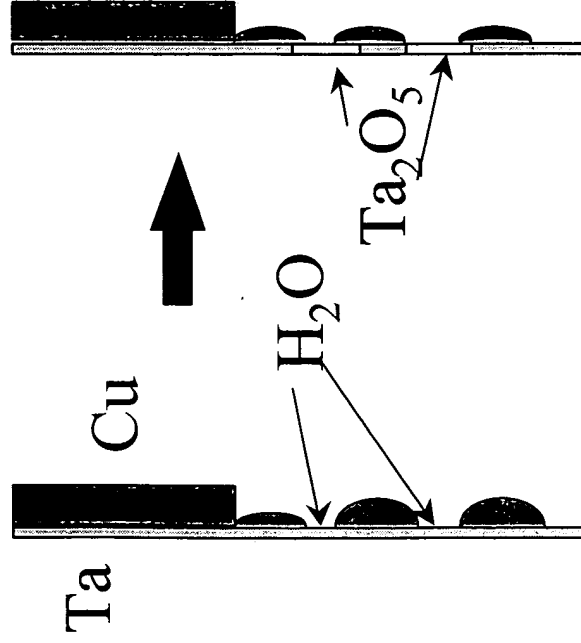
$$D = 1.0 \times 10^{-6} \text{ cm}^2 / \text{sec}$$

$$F = \frac{D \Delta C}{\delta} = 1 \times 10^{-10} \text{ M} / \text{sec cm}^2 = 0.7 \times 10^{14} \text{ molecules} / \text{sec cm}^2$$

$$t_{\text{abs}} = 1 \times 10^{15} \text{ molecules} / \text{cm}^2 / 0.7 \times 10^{14} \text{ molecules} / \text{sec cm}^2 = 14 \text{ sec}$$

FIG. 17

How Would Ta_2O_5 be Formed in the Side Walls?



Conclusions: Formation of Ta_2O_5 is anticipated (thermodynamics)'

Question: How much of the Ta is expected to be converted to the electrically insulating oxide?

FIG. 18

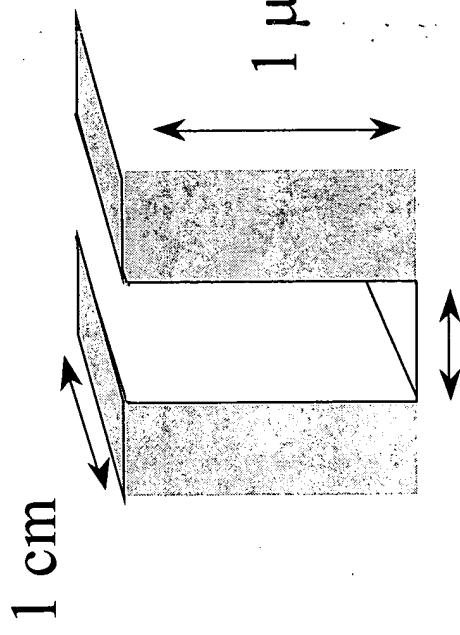
$i = i_a$
High C
 $R_{ct} = \frac{\eta_{ct}}{i}$
 1. The surface

$$\begin{aligned} \text{High Current} \quad R_{ct} &= \frac{\eta_{ct}}{i} \approx \frac{\eta_{ct}}{i_o e^{-\alpha n f \eta_{ct}}} \\ \text{Low Current} \quad R_{ct} &= \frac{\eta_{ct}}{i} \approx \frac{1}{i_o n F} \end{aligned}$$

- # When is R_f significant ?

FIG. 19

Electrical Resistances and Filling of Small Features



$$w = 0.25 \mu$$

$$R = \frac{\rho L}{2A} = 4 \text{ m}\Omega, 50 \text{ k}\Omega$$

$$\Delta V = IR = (iw)R$$

$$\Delta V_{\text{Ta}} = 1 \times 10^{-9} \text{ to } 5 \times 10^{-6} \text{ V}$$

$$\Delta V_{\text{Ta}_2\text{O}_5} = 0.003 \text{ to } 0.16 \text{ V}$$

Assumptions

1. Only Ta or TaO₂ (2 nm thick) is present on side wall for electrical conductivity
2. Plating occurs only at bottom of trench at 10-500 mA/cm² (conformal vs fast bottom-up fill rates).

$$\rho_{\text{Ta}} = 16 \times 10^{-6} \Omega \text{ cm}, \rho_{\text{Ta}_2\text{O}_5} = 50 \Omega \text{ cm}$$

Conclusions

1. If sidewall metallic Ta of 2 nm is present in the feature, electrical resistivity is insignificant.
2. If sidewall material is cracked, exposed to oxygen and converted to TaO₂, the electrical resistance in the film will be too large to support bottom-up filling.

FIG. 20

Nucleation Phenomena

$$\Delta G_i = \pi r^2 (2\sigma_{13} + \sigma_{12} - \sigma_{23}) + \frac{2}{3} \pi r^3 \Delta G_v$$

$$\frac{\Delta G_i}{v_m} = \frac{3 (2\sigma_{13} + \sigma_{12} - \sigma_{23})}{2v_m r} + \Delta \overline{G}_v$$

$$E(r) = \frac{RT}{nF} \ln \left[\frac{3 (2\sigma_{13} + \sigma_{12} - \sigma_{23})}{2v_m r} + \Delta \overline{G}_v \right]$$

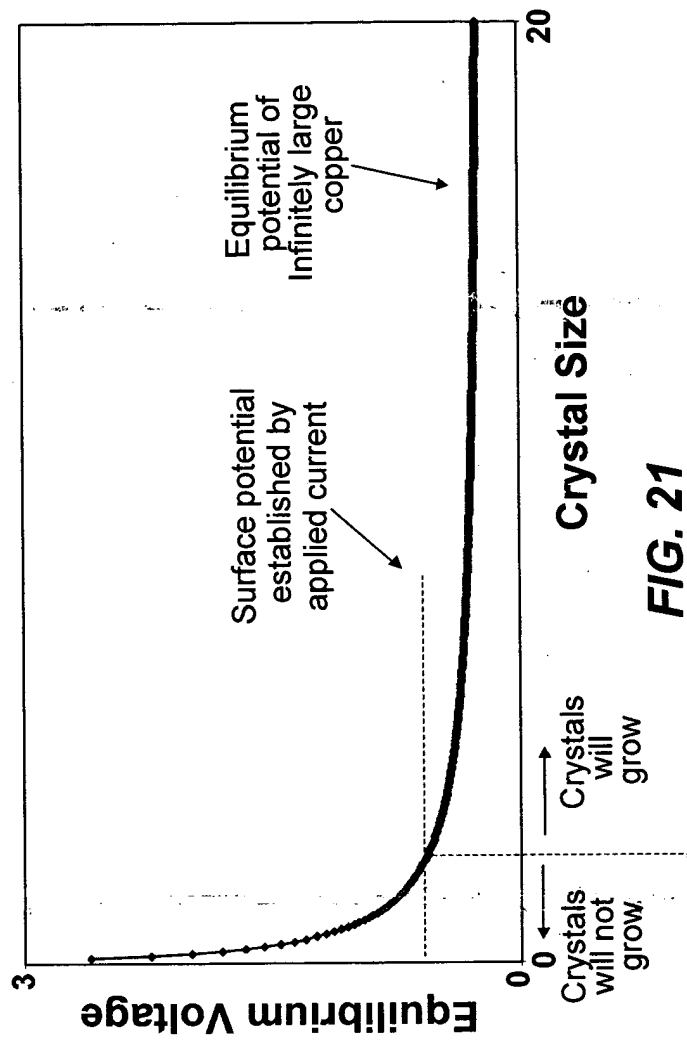
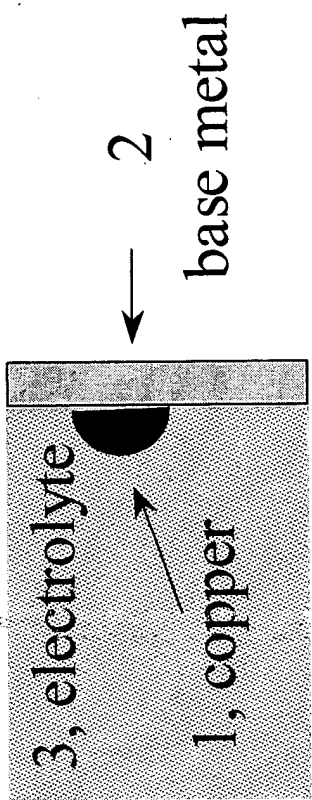
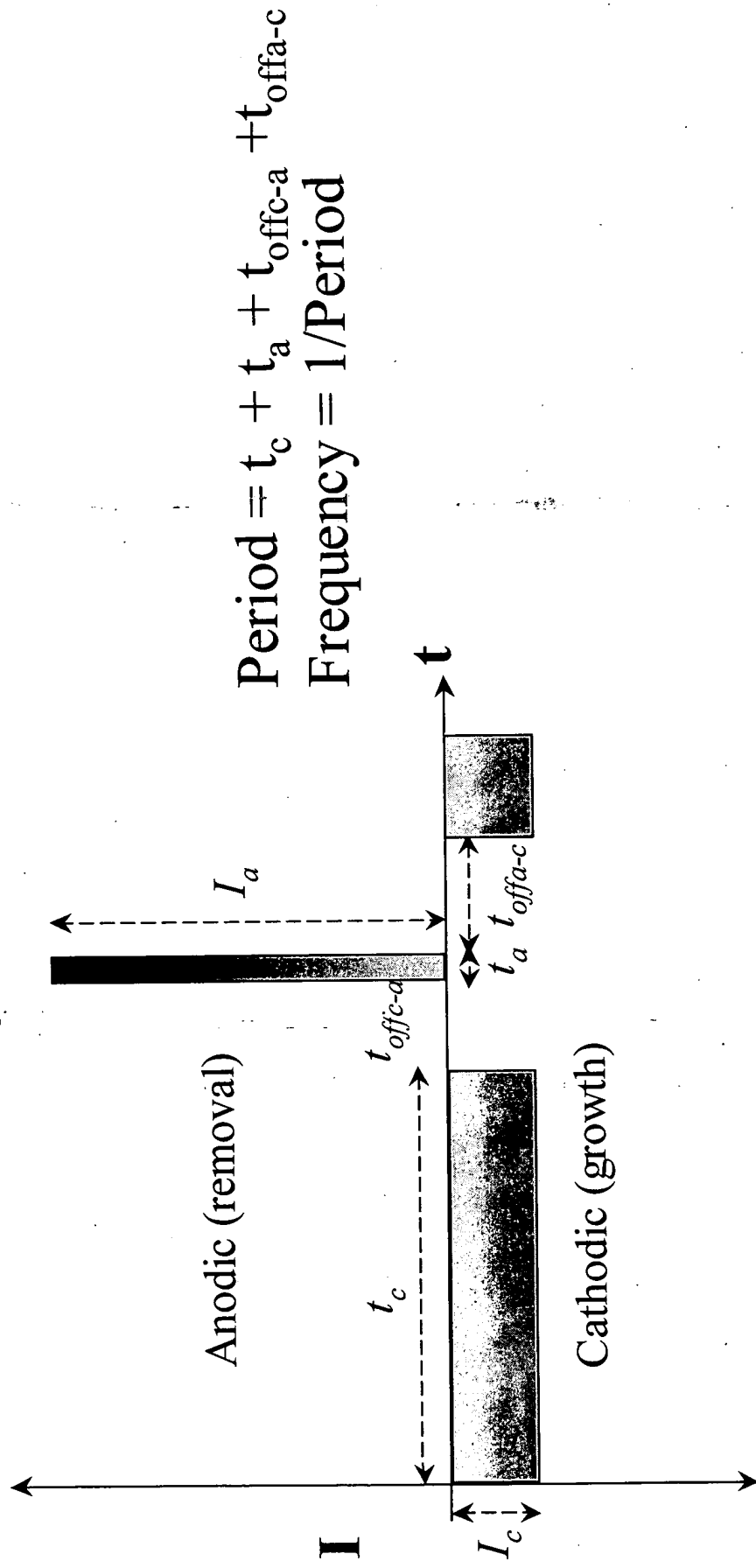


FIG. 21

Bipolar Pulse Plating Waveform

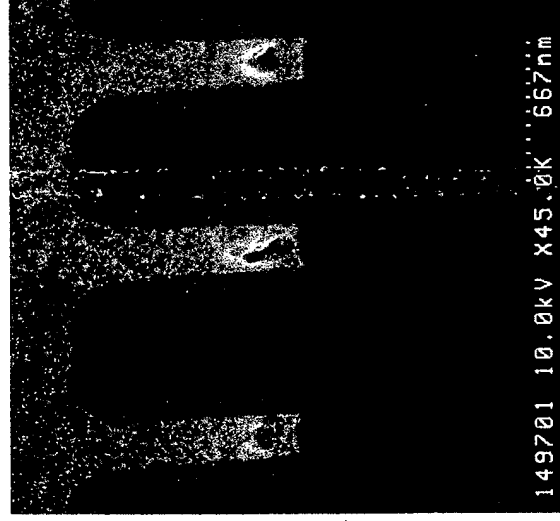


Constraint: $I_c \cdot t_c - I_a \cdot t_a > 0$

FIG. 22

Bipolar pulse plating: Phase 1-waveform screening

- ◆ Select tests done on SEMATECH backfilled vias (Apr 98, 3)
- ◆ Bipolar pulse with hi anodic current showed improvement over POR
- ◆ Eliminated other pulse waveforms



POR 1.0, 7A DC



10A Cathodic, 80 A Anodic,
125 Hz, 10 msec t_{off}

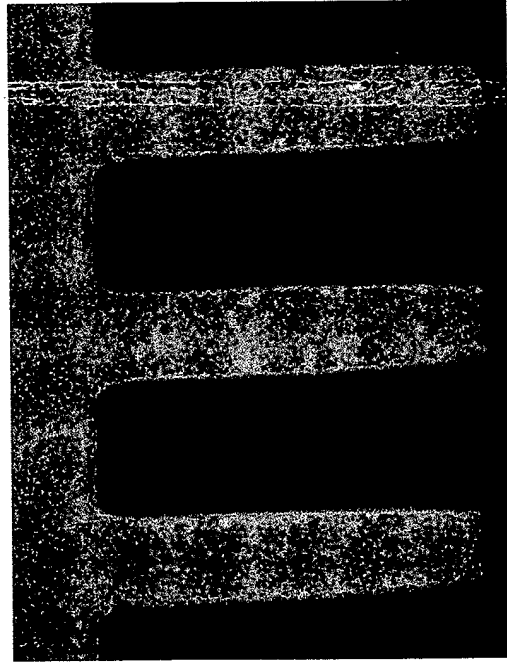
FIG. 23

Bipolar pulse plating: Phase2-Trench optimization

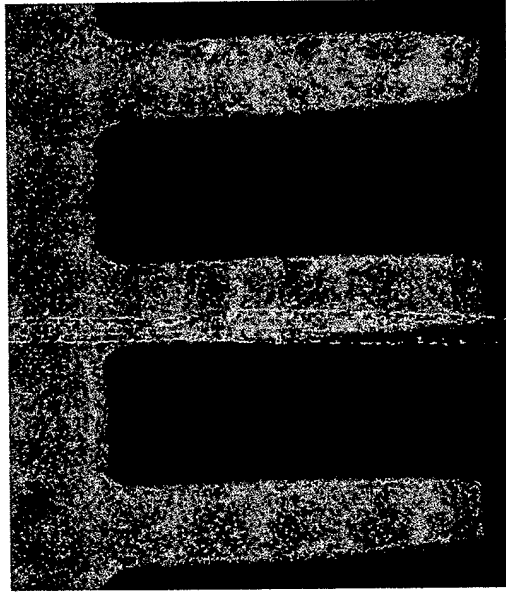
- ◆ **1"x1" SEMATECH backfilled trenches with HCM- α seed taped on 8" wafers (52)**
- ◆ **2 types of waveforms tested**
- ◆ **No pulsed waveform resulted in better fill than POR 1.0**
- ◆ **Higher pulsed anodic currents improved top filling**
- ◆ **Lower pulsed cathodic current improved filling**
 - longer on-times were better
- ◆ **Need to perform tests with initiation on vias**

FIG. 24

Fill Improvement: Reverse pulse matrix



A



Field 5, 0.34 μm , AR = 4.5 B

Pulse Matrix			
#	Ic	t _c /t _a ratio	Freq (Hz)
A	4	25	10
B	4	25	10

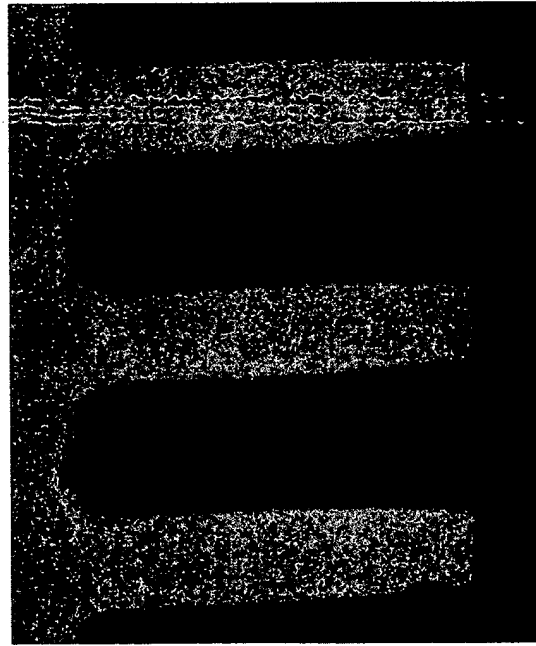
- Feature: SEMATECH Standard vias
- Seed: 1600Å HCM Cu/250Å HCM Ta
- Plate: Step 1: 0.25A DC, 50 sec
Step 2: Pulse



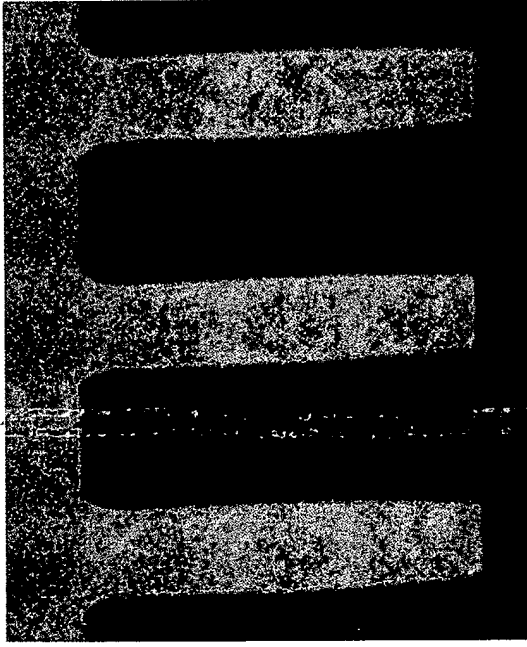
Control, 7A DC

FIG. 25

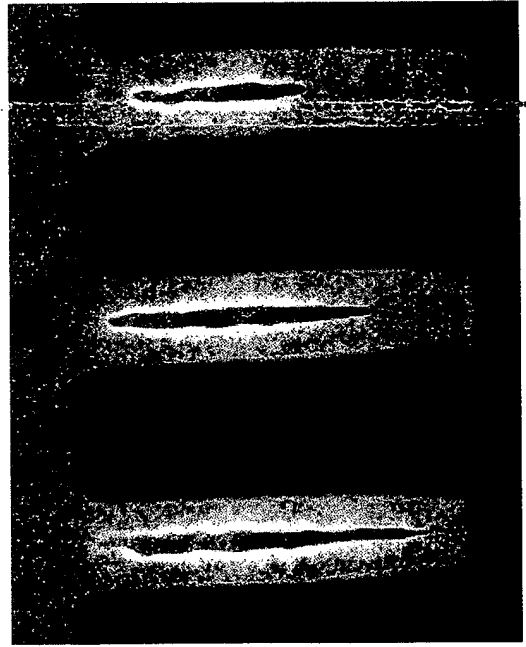
Fill Improvement: Reverse pulse matrix



A



B



Control, 7A DC

Pulse Matrix			
#	Ic	t _c /t _a ratio	Freq (Hz)
A	4	24	100
B	4	22	100
			Toff
			0
			3

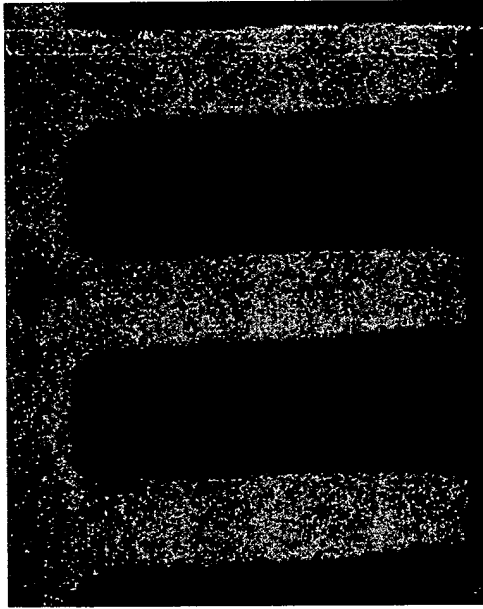
- Feature: SEMATECH Standard vias, Field 5, 0.34 μm , AR = 4.5
- Seed: 1600Å HCM Cu/250Å HCM Ta
- Plate: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

FIG. 26

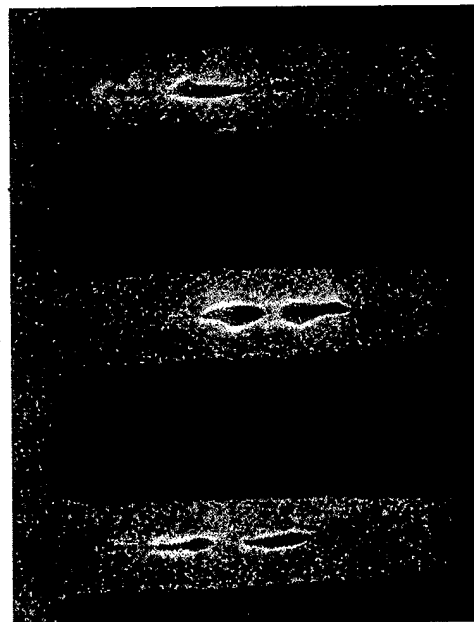
Reverse pulse matrix: Impact of t_c/t_a ratio/freq.



A



B



C



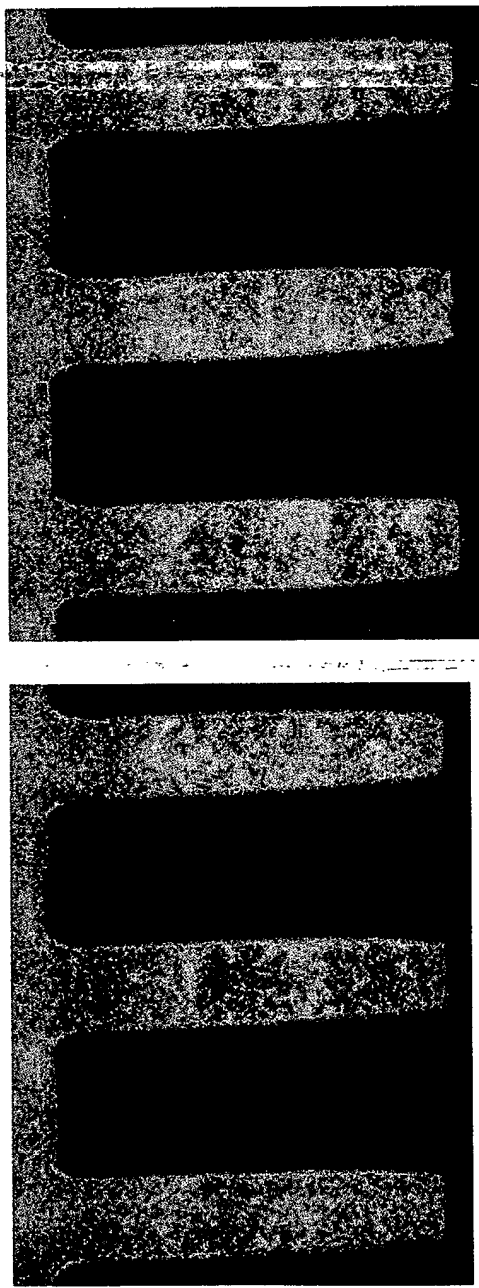
D

<p>•Feature: SEMATECH Standard vias, Field 5, 0.34 μm, AR = 4.5</p> <p>•Seed: 1600Å HCM Cu/250Å HCM Ta</p> <p>•Plate: Step 1: 0.25A DC, 50 sec</p>	<p>Step 2: Pulse</p>
--	----------------------

Pulse Matrix			
#	Ic	t_c/t_a ratio	Freq (Hz)
A	4	25	10
B	4	25	100
C	4	49	10
D	4	49	100
			Toff
			0
			0
			0
			0

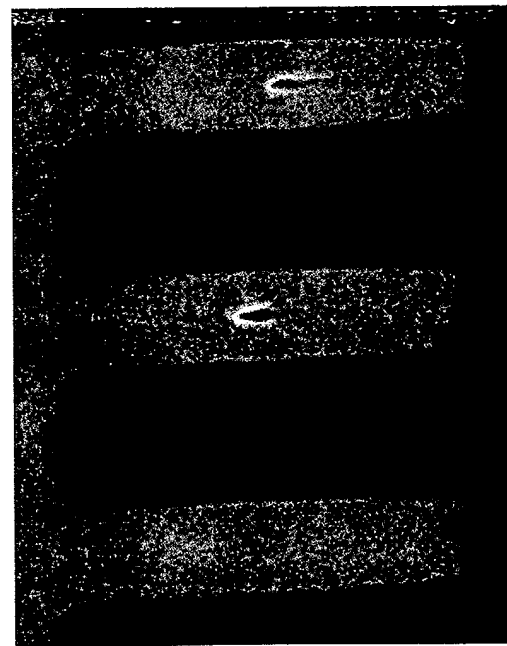
FIG. 27

Reverse pulse matrix: Impact of t_c/t_a ratio/freq.

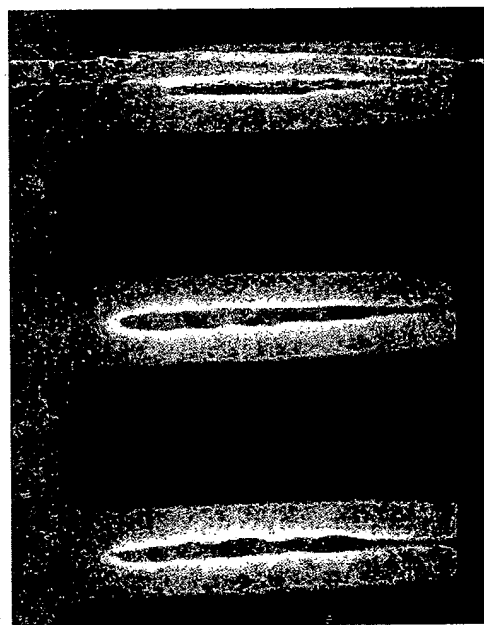


A

B



C



D

FIG. 28

•**Feature:** SEMATECH
Standard vias, Field 5, **0.34**
μm, **AR = 4.5**
•**Seed:** 1600Å HCM
Cu/250Å HCM Ta
•**Plate:** Step 1: 0.25A DC,
50 sec
Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	25	10	3
B	4	25	100	3
C	4	49	10	3
D	4	49	100	3

Reverse pulse matrix: Impact of t_c/t_a ratio

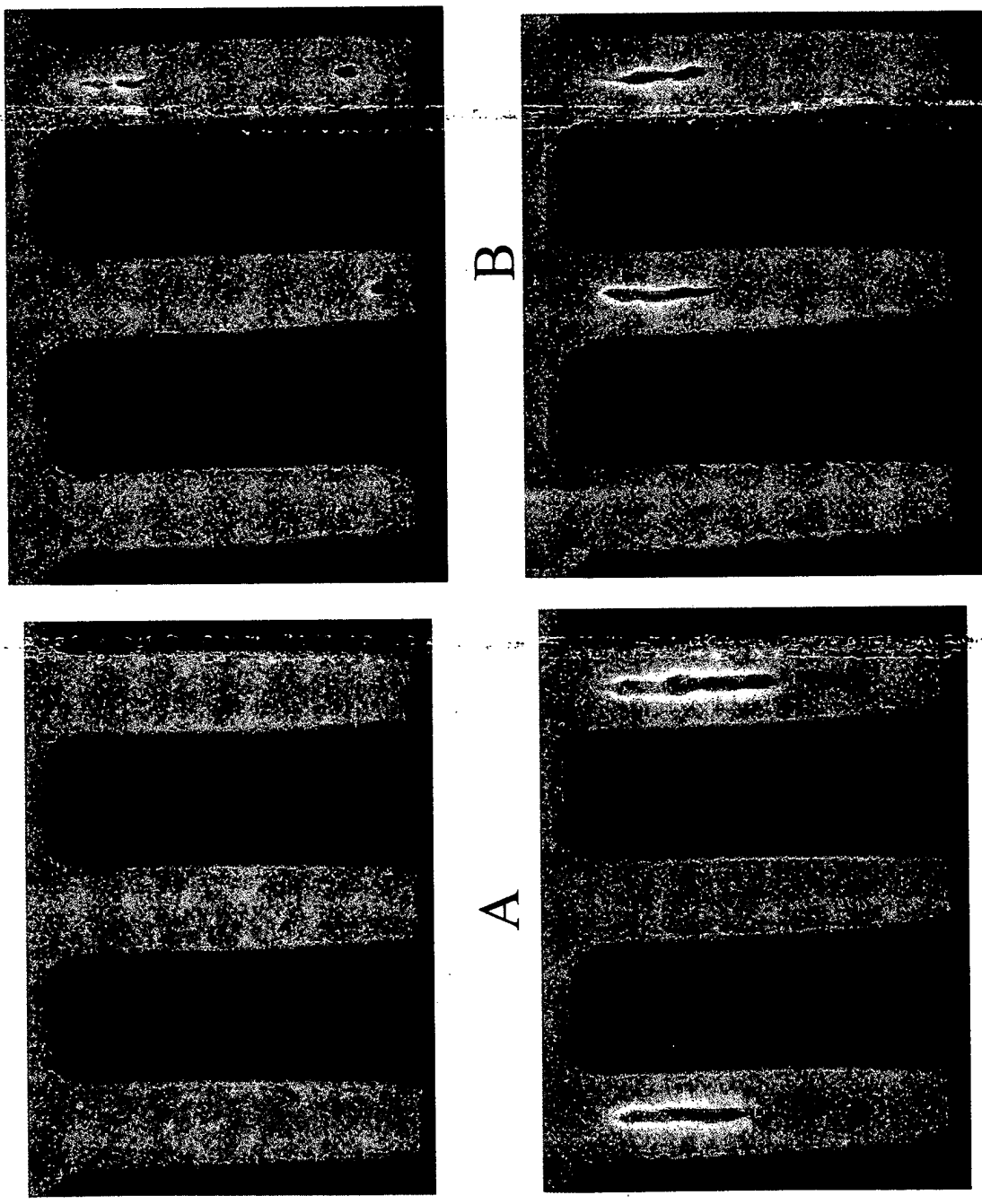
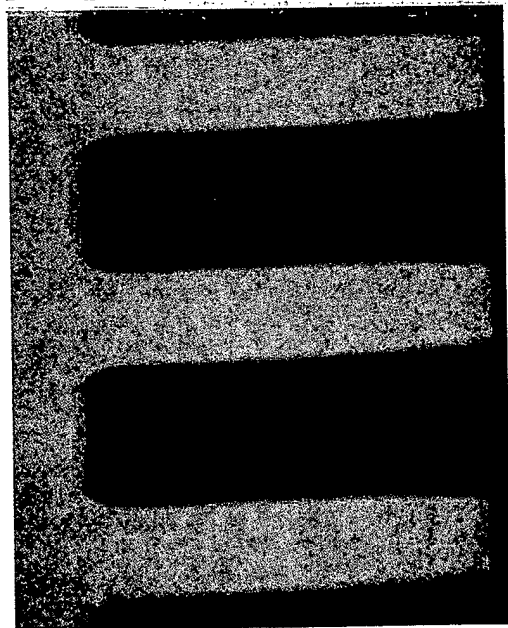


FIG. 29 D

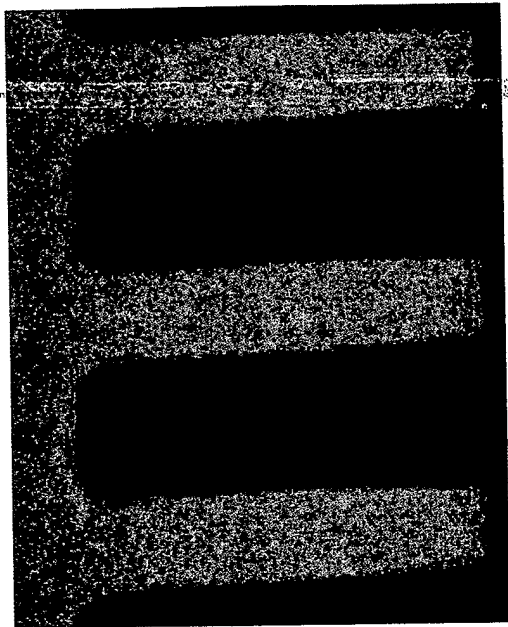
•Feature: SEMATECH
 Standard vias, Field 5, **0.34**
 μm , **AR = 4.5**
•Seed: 1600Å HCM
 Cu/250Å HCM Ta
•Plate: Step 1: 0.25A DC,
 50 sec
 Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
C	8	25	10	0
D	8	25	10	3
C	8	49	10	0
D	8	50	10	3

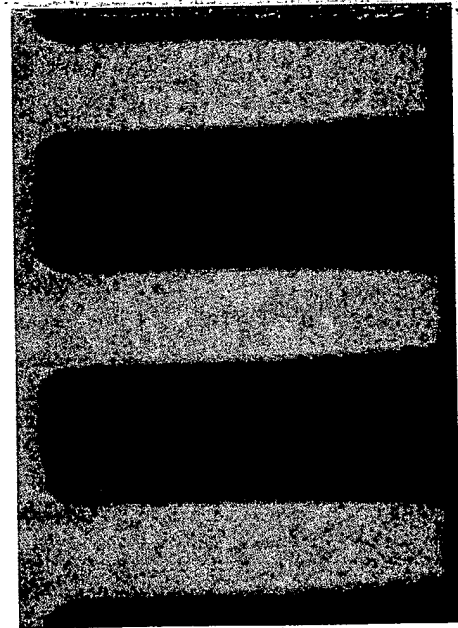
Reverse pulse matrix: Impact of cathodic current/freq.



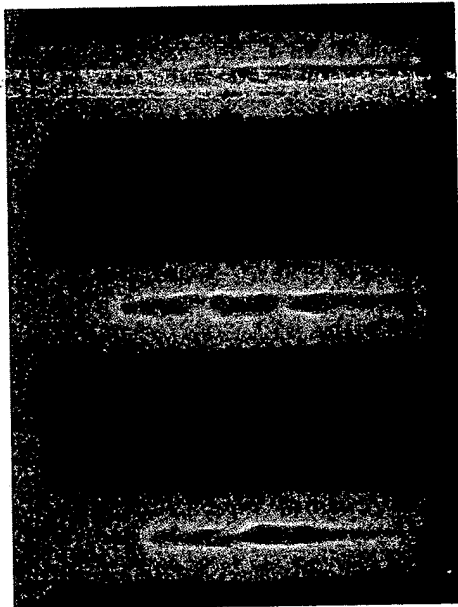
A



B



C

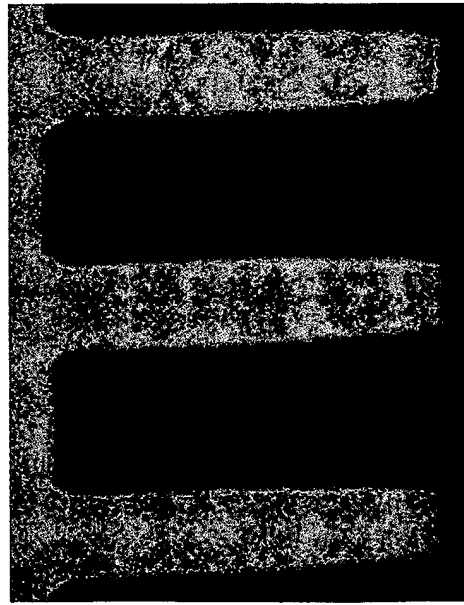


D

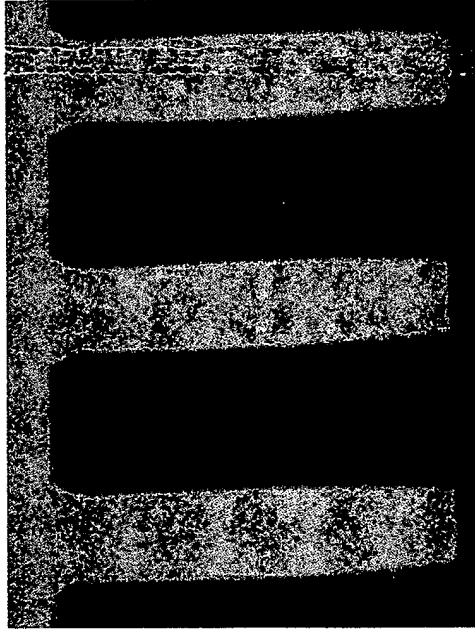
•*Feature:* SEMATECH
Standard vias, Field 5, 0.34
 μm , AR = 4.5
•*Seed:* 1600Å HCM
Cu/250Å HCM Ta
•*Plate:* Step 1: 0.25A DC,
50 sec
Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	25	10	0
B	4	25	100	0
C	8	25	10	0
D	8	25	100	0

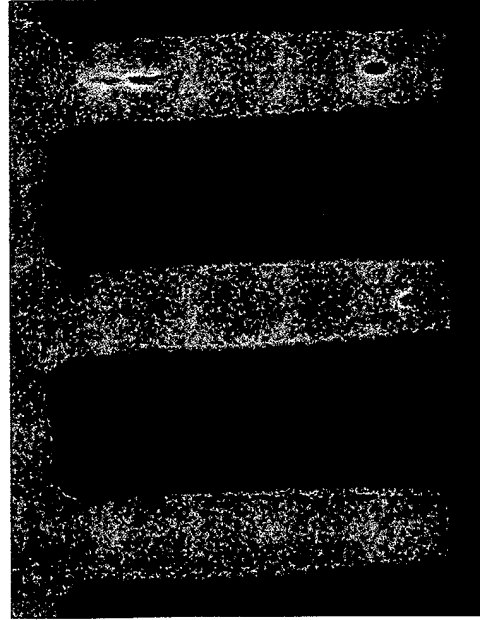
Reverse pulse matrix: Impact of cathodic current/freq.



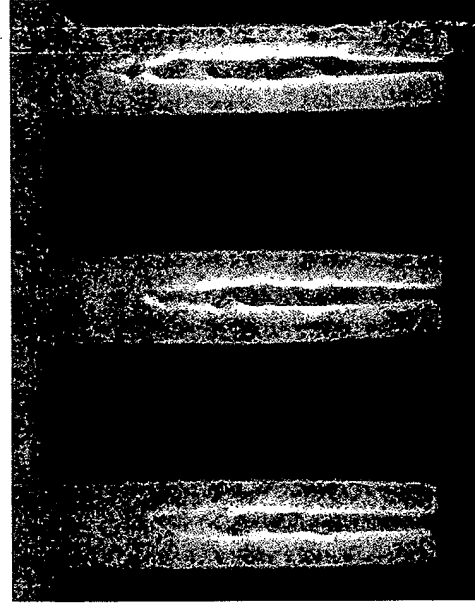
A



B



C



D

•Feature: SEMATECH

Standard vias, Field 5, **0.34**
μm, AR = **4.5**

•Seed: 1600Å HCM

Cu/250Å HCM Ta

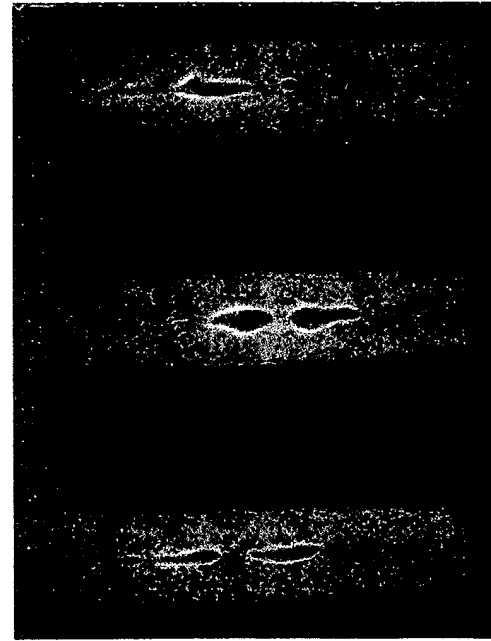
•Plate: Step 1: 0.25A DC,
50 sec

Step 2: Pulse

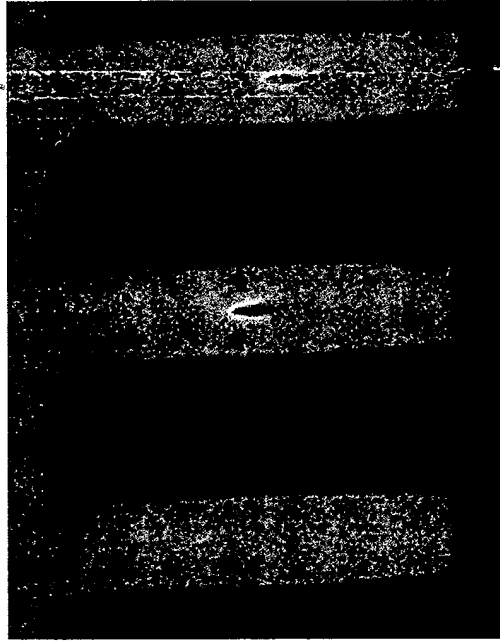
Pulse Matrix				
#	Ic	t _c /t _a ratio	Freq (Hz)	Toff
A	4	25	10	3
B	4	25	100	3
C	8	25	10	3
D	8	25	100	3

FIG. 31

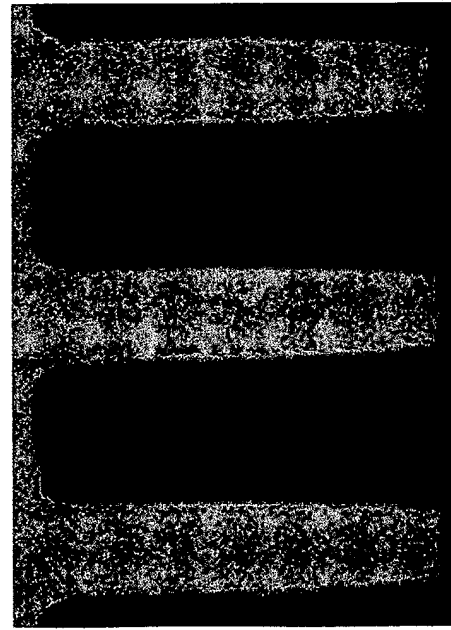
Reverse pulse matrix: impact of cathodic current/off time



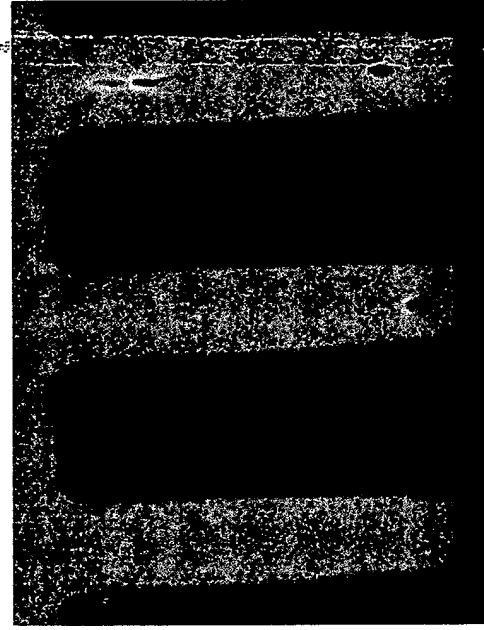
A



B



C



D

•Feature: SEMATECH
 Standard vias, Field 5, **0.34**
 μm , AR = **4.5**
•Seed: 1600Å HCM
 Cu/250Å HCM Ta
•Plate: Step 1: 0.25A DC,
 50 sec
 Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	49	10	0
B	4	49	10	3
C	8	25	10	0
D	8	25	10	3

FIG. 32

Reverse pulse matrix:

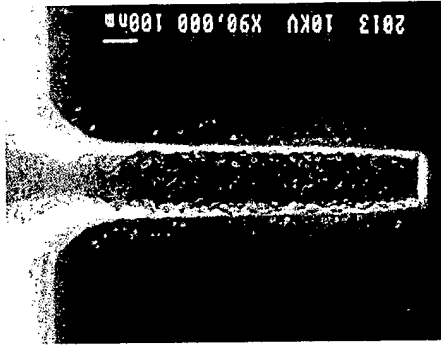
- ◆ **Reverse pulse shows superior fill compared to DC alone**
 - Low current initiation necessary
 - Smallest features filled (0.34 μ m, 4.5 AR)
- ◆ **Initial data indicates longer reverse pulse time yields better fill**
- ◆ **100 Hz clearly shows poorer fill than 10 Hz**
- ◆ **Off time impact not clear**
- ◆ **5:1 AR Via structure breakpoint**
 - Initiation limit-cannot overcome seed deficiency
 - Observed in backfilled via fill (Field 4, 0.21 μ m, 5:1 AR) also

Center voids eliminated on wafer edge and center by reverse pulse plating

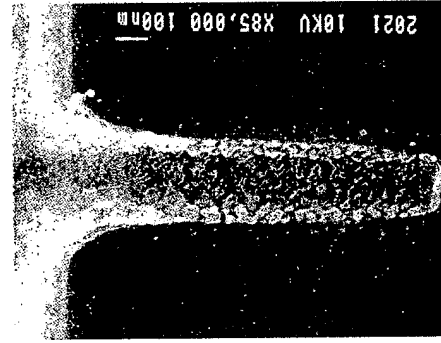
FIG. 33

HCM vs. IMP Seed Comparison on Backfilled Vias

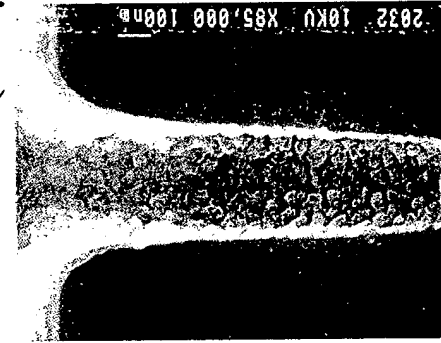
Field 4(.21μ)



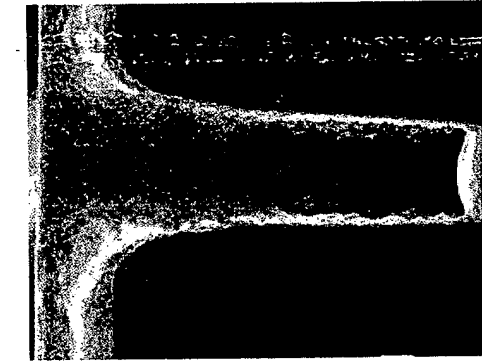
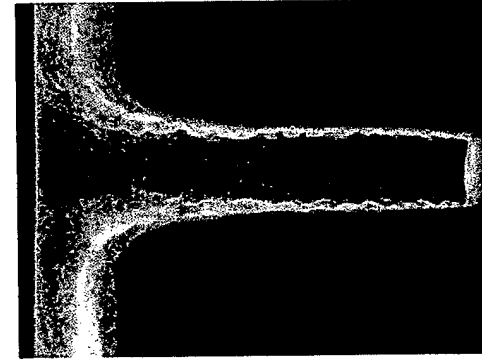
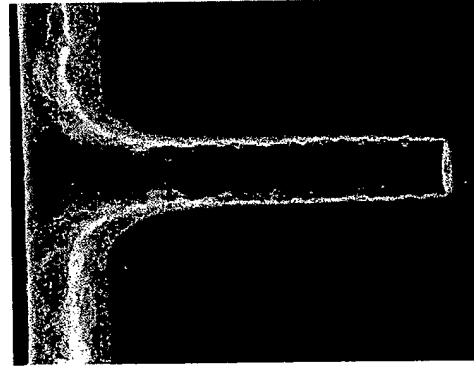
Field 3(.25μ)



Field 1(.30μ)



IMP



HCM
POR6

FIG. 34

Note: 300 Å Ta + 2400 Å Cu

Current Sweep Experimental Matrix #1

Experiment Number	Initial Current (A)	Maximum Current (A)	Time to Max Current (s)	Time at Max Current (s)	Current Sweep (mA/sec)	Total Equiv. Deposition Thick (Å)
1	0.1	2	25	82	76	2511
2	0.1	4	75	9	52	2505
3	0.1	4	60	17	65	2521
4	0.1	2	60	64	32	2521
5	0.25	2	50	68	35	2538
6	0.25	4	90	0	42	2525
7	0.25	4	45	24	83	2529
8	0.25	2	90	45	19	2525

FIG. 35

Current Sweep Experimental Matrix #1

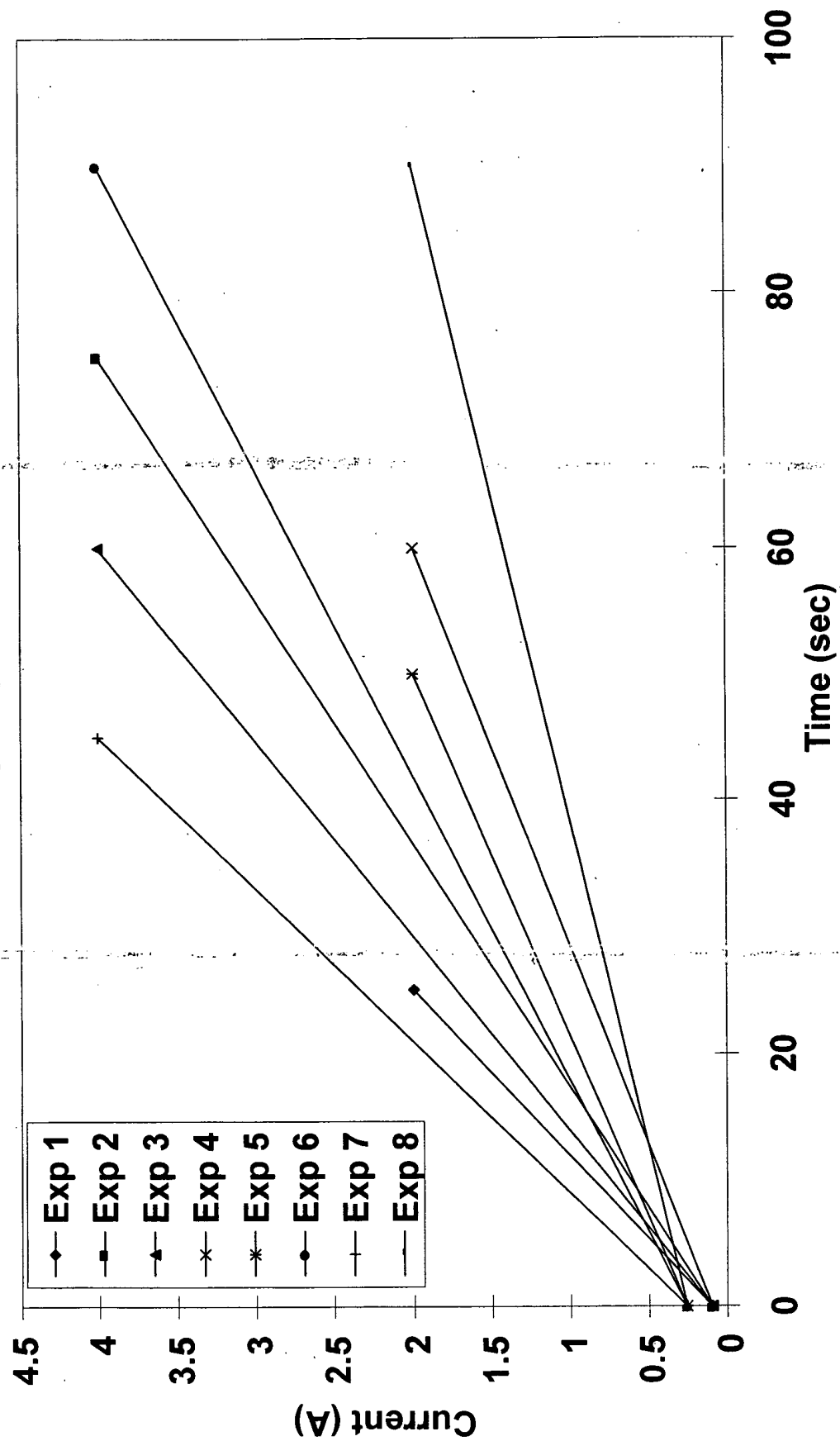
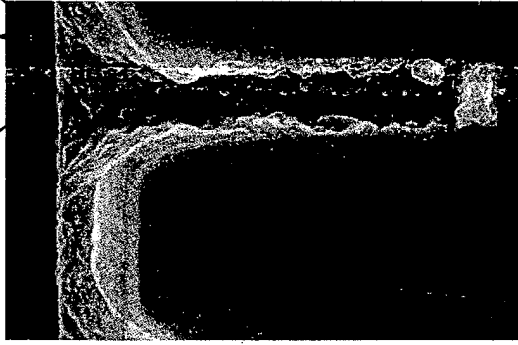


FIG. 36

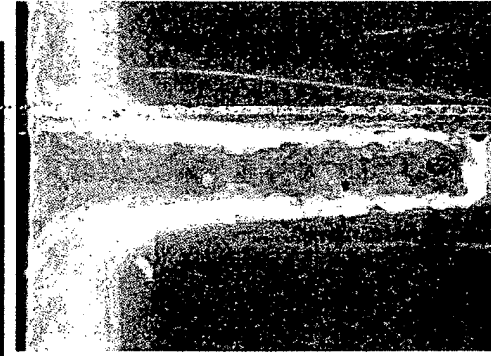
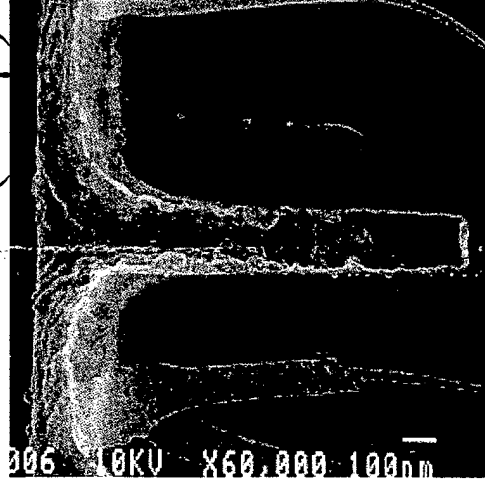
Comparison: .5 Amp to .1 Amp Initiation

Field 3 (.25 μ)

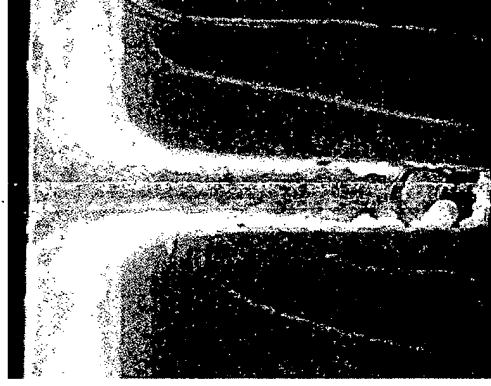


.1 A
100s

Field 4 (.21 μ)



.5 A
22.5s



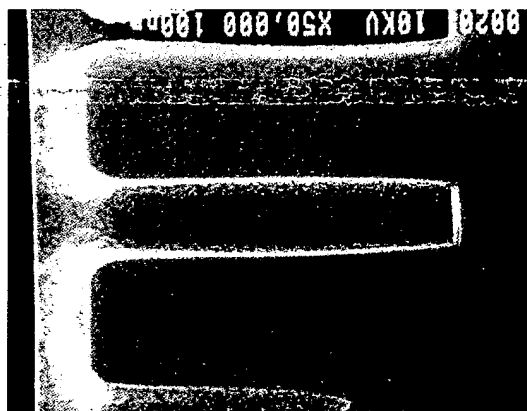
Note: HCM POR6, 300 Å Ta + 2400 Å Cu

FIG. 37

Impact of induction time



0.34 μm, AR 3.9



0.55 μm, AR 3.0



HCM

Cu/Ta

1600 Å Cu

/250 Å Ta

Conclusion

- Induction removes critical seed layer

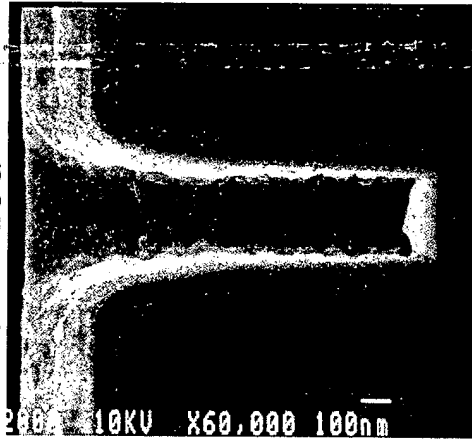
HCM seed only

After 2 sec induction

FIG. 38

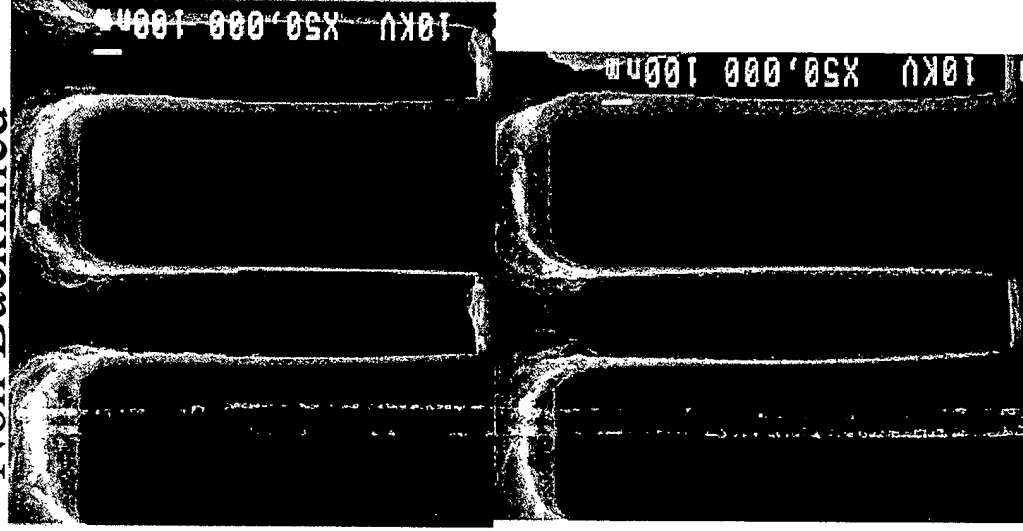
Induction Comparison: Backfilled vs. Non-backfilled Vias

Backfilled

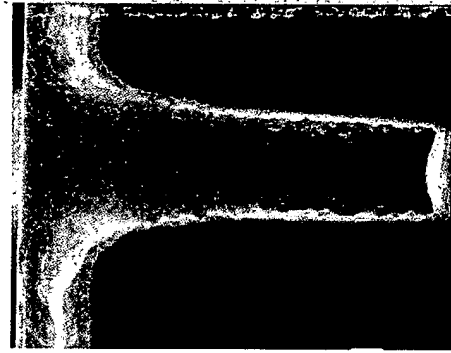


2 sec
Ind.

Non-Backfilled



Seed
Only

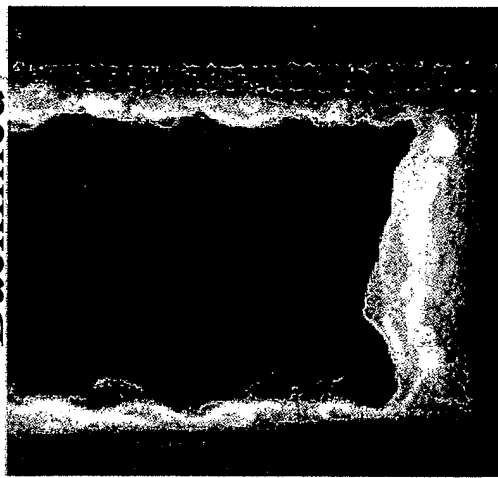


Note: HCM POR6 seed (2000-2400 Å), .3μ wide

FIG. 39

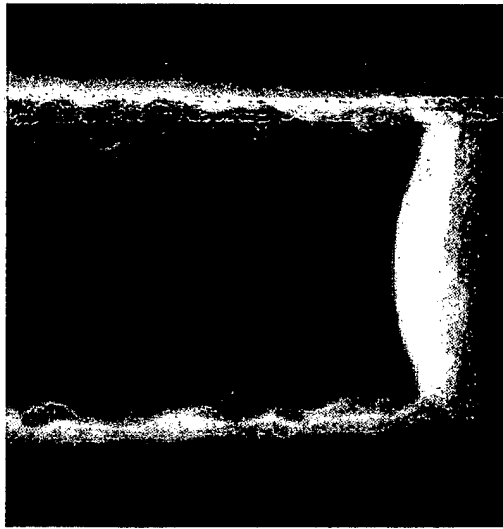
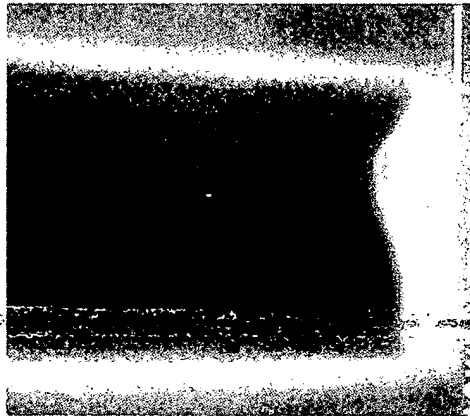
Induction Comparison: Backfilled vs. Non-Backfilled Vias

Backfilled

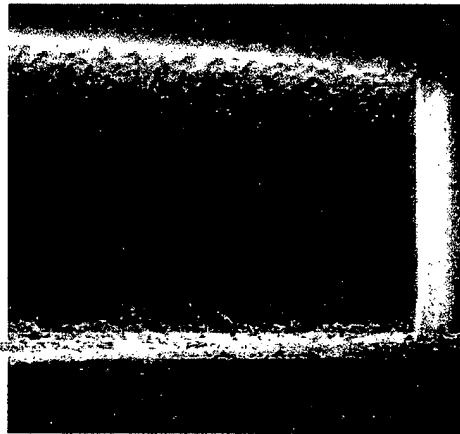


2 sec
Ind.

Non-Backfilled



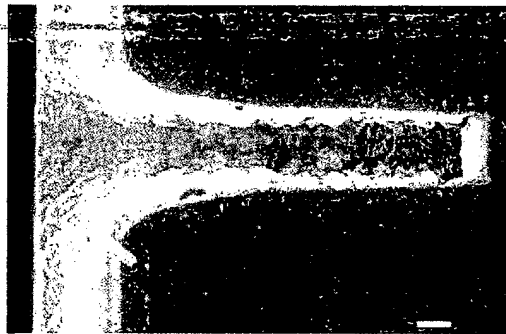
Seed
Only



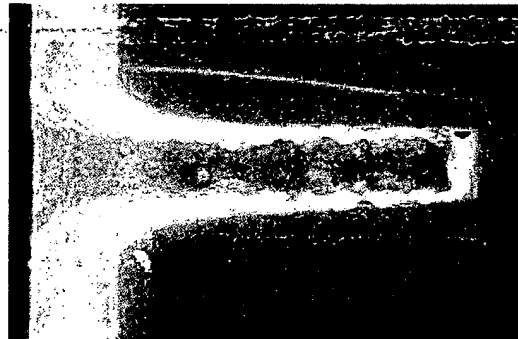
Note: HCM POR6 seed (2000-2400 Å), .3μ wide

FIG. 40

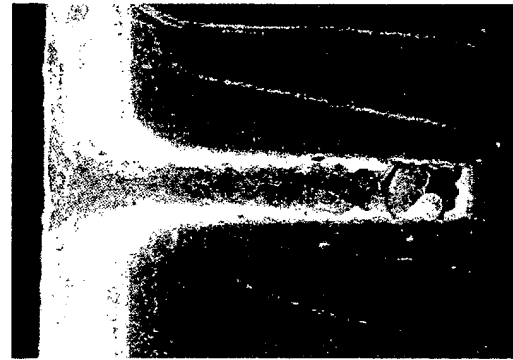
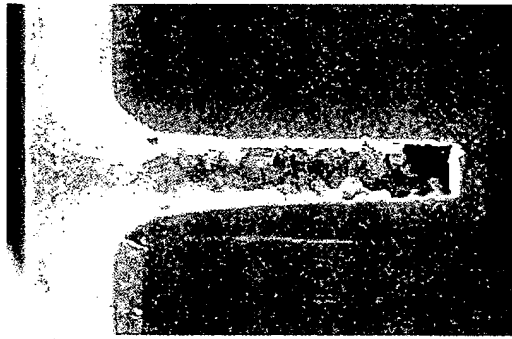
Initiation profile-Conformality



0.5 A, 7.5 sec



0.5 A, 22.5 sec



0.25 μm , 4.8 AR

0.21 μm , 4.0 AR

FIG. 41

- HCM Cu/Ta
- 1600 Å Cu
- /250 Å Ta

Conclusion

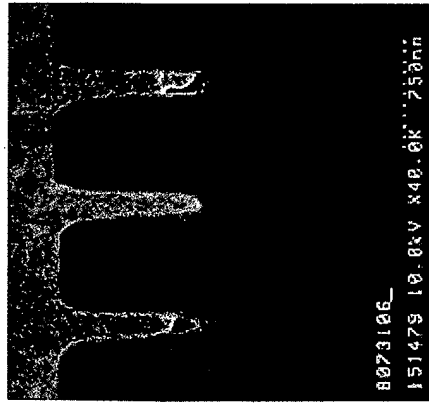
- Conformal growth even at small features

Unipolar Pulse Tests: 0.18 μ Via Wafers

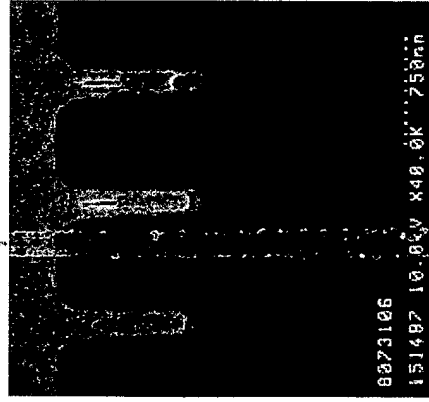
Wafer Id	Seed Thick	Induction Time	Initiation Time	Initation Conditions	Fill Time	Fill Current
3106-03	1600 Å	0 seconds	8 seconds	5% 20 A 0.5A DC	15 seconds	7 A
3106-04	1600 Å	0 seconds	8 seconds	2%, 50A 0.5A DC	15 seconds	7 A
3106-05	1600 Å	0 seconds	16 seconds	5% 20 A 0.5A DC	15 seconds	7 A
3106-06	1600 Å	0 seconds	16 seconds	2%, 50A 0.5A DC	15 seconds	7 A
3106-08	1600 Å	0 seconds	16 seconds	5% 20 A	15 seconds	7 A

FIG. 42

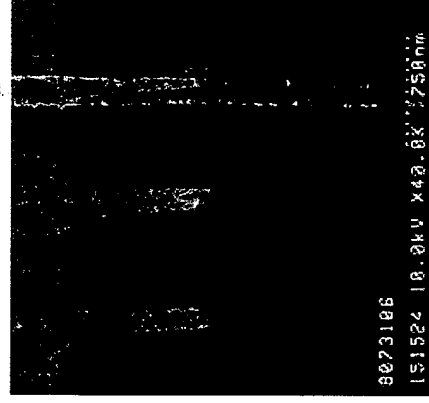
Unipolar Pulse = DC Initiation: Field 4



8 sec, 5% 20A



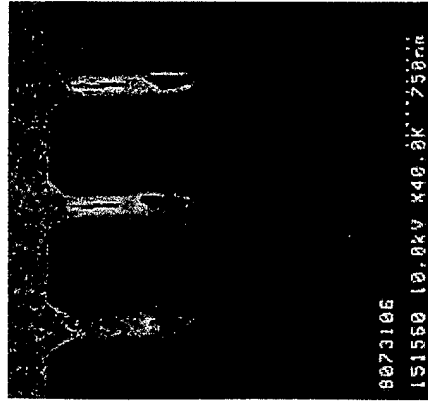
8 sec, 2% 50A



16 sec, 5% 20A



16 sec, 2% 50A



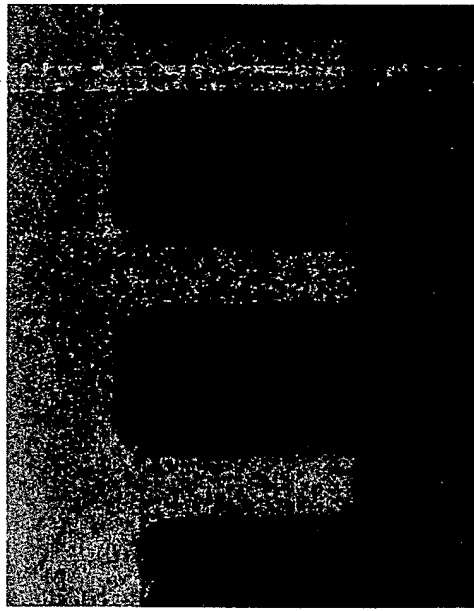
16 sec, 2% 50A

No DC background

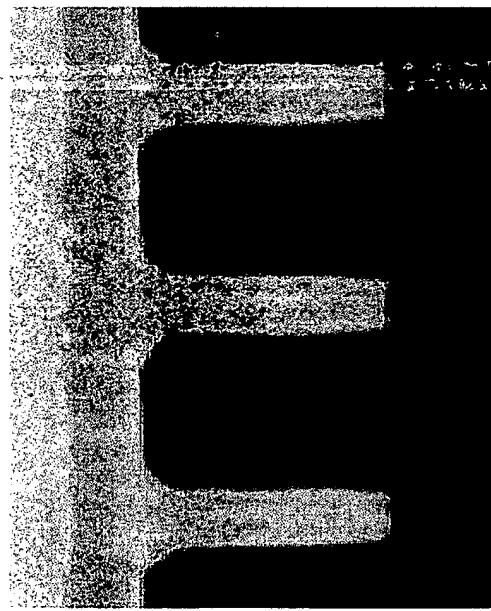
-DC background current of 0.5A during initiation
-DC Fill of 7A for 15 seconds

FIG. 43

Initiation + Fill



0.5 A, 7.5 sec



0.5 A, 22.5 sec



0.25 μm , 4.8 AR

0.21 μm , 4.0 AR

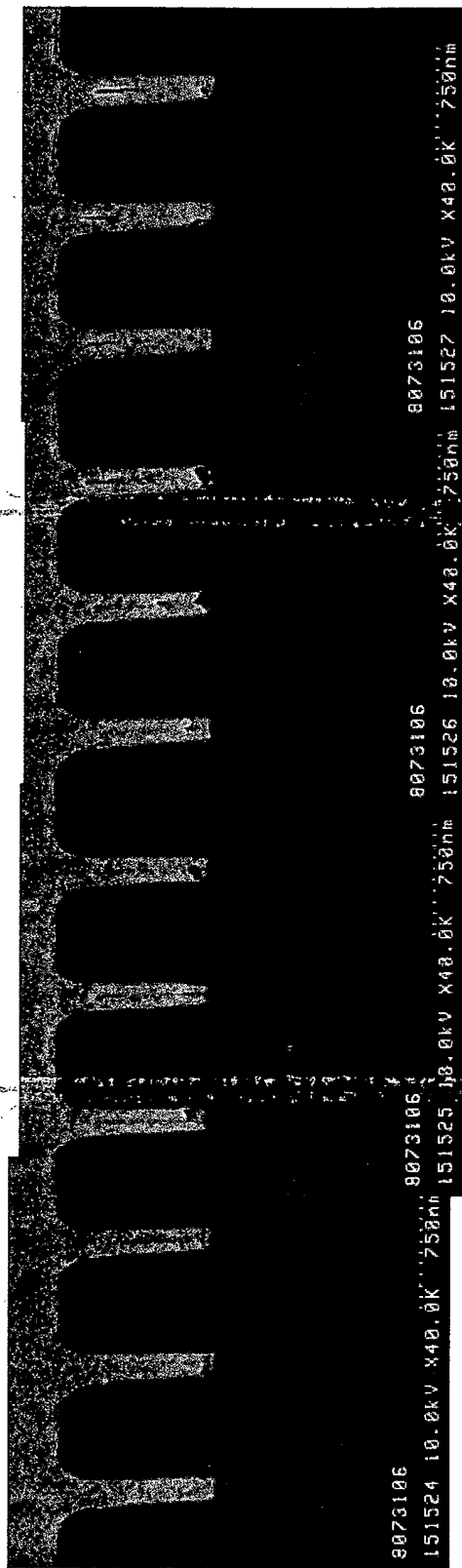
FIG. 44

- HCM Cu/Ta
- 1600 Å Cu
- /250 Å Ta

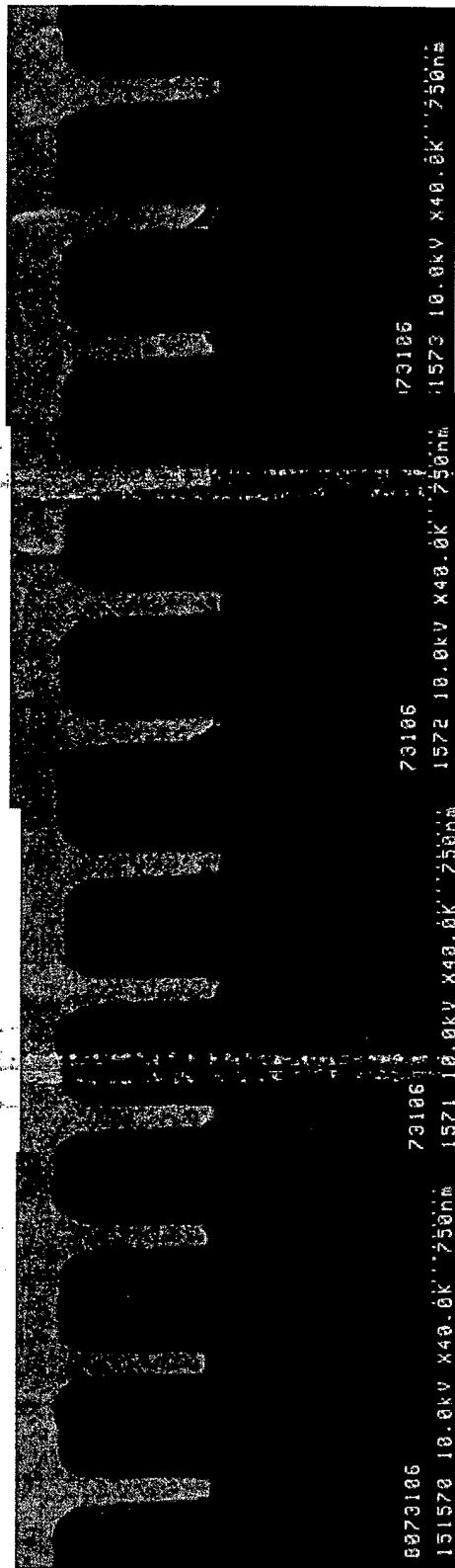
Conclusion

- *Initiation does not build seed at the bottom sidewall*
- *Correlates to final void formation*

Comparison of 0.5 A Initiation: Unipolar Pulsing Conditions



16 sec, 5% 20A



16 sec, 2% 50A

FIG. 45

Comparison of 0.5 A Initiation: With and Without Unipolar Pulsing

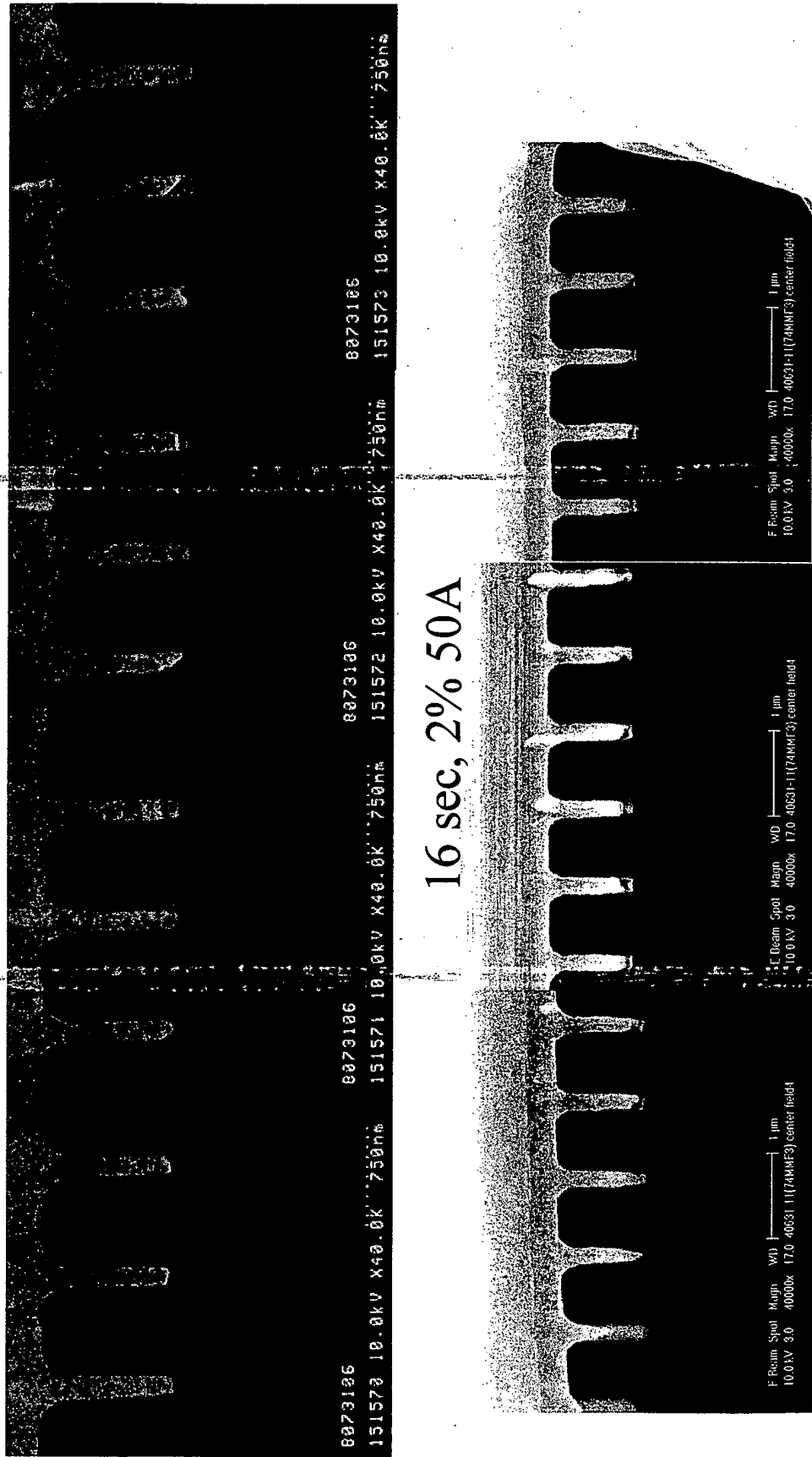
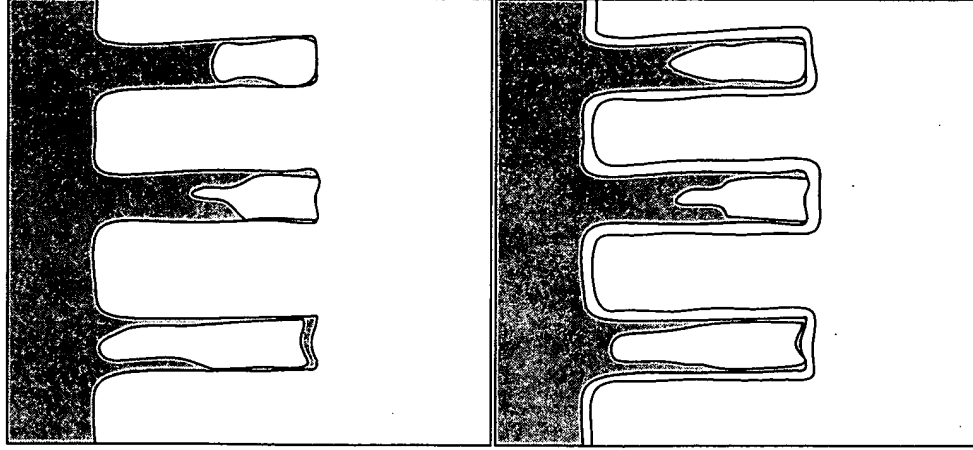


FIG. 46

Without Initiation: IMP seed:



- ◆ SEMATECH Backfilled via, Field 3, 0.24 μm x 1.13 μm , AR = 4.7
- ◆ Bottom Voids - Yes
- ◆ Side wall Voids - No
- ◆ Top Void - No
- ◆ Center Seam - No
- ◆ Film nucleation - poor
- ◆ Void % = 90%
- ◆ 2 second induction

Barrier/Seed Layer

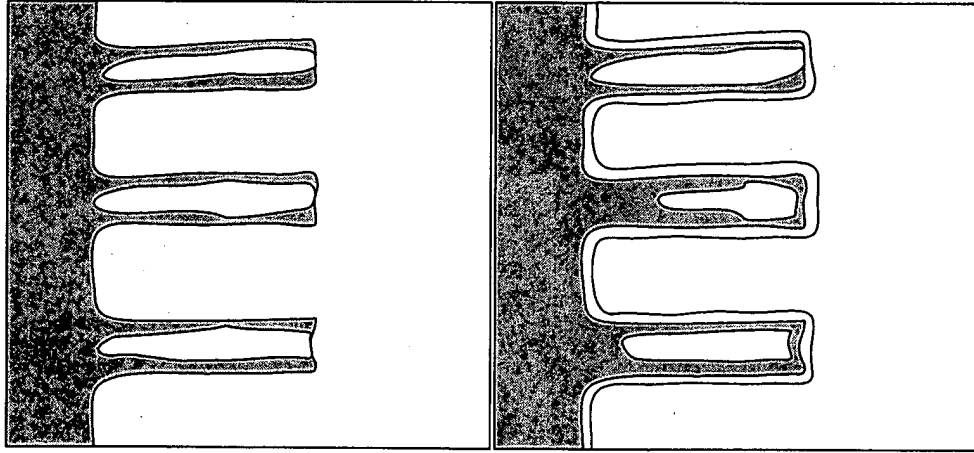
-IMP
-250Å Ta/1600Å Cu
-Degas Temp.?
-Sputter etch thickness:?
-wafer bias:?

Electroplating

-DC 7 A
Bath Conditions
[Cu²⁺] = 17.3 g/l H₂SO₄ = 176 g/l
[MLO] = 3 ml/l [MD] = 8 ml/l
[Cl⁻] = 55 ppm Temp = 22°C
Flow = 8 lpm RPM: 125

FIG. 47

Without Initiation: IMP seed:



- ◆ SEMATECH Backfilled via, Field 3, 0.24 μm x 1.13 μm , AR = 4.7
- ◆ Bottom Voids - Yes
- ◆ Side wall Voids - No
- ◆ Top Void - No
- ◆ Center Seam - No
- ◆ Film nucleation - poor
- ◆ Void % = 70%
- ◆ 2 second induction

Barrier/Seed Layer

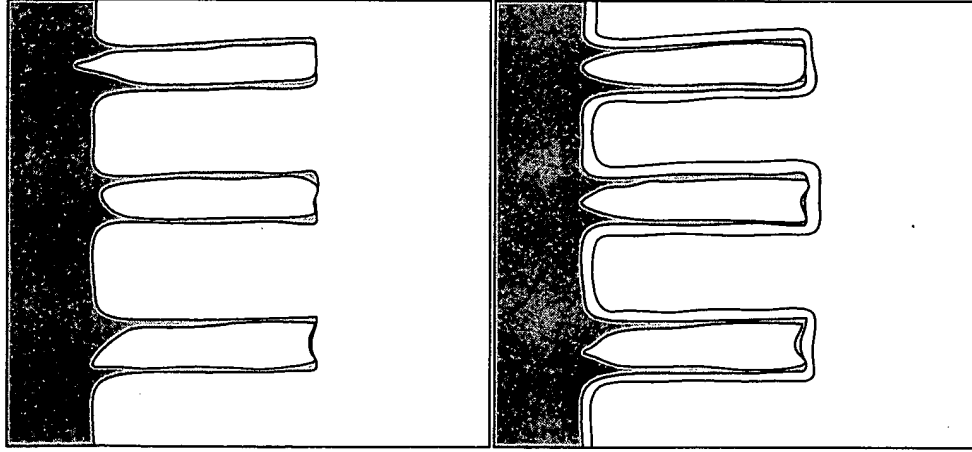
- IMP
- 250Å Ta/2200Å Cu
- Degas Temp.?
- Sputter etch thickness:?
- wafer bias:?

Electroplating

- DC 1 A, 15 sec then 7 A
- Bath Conditions
- [Cu^{+2}] = 17.3 g/l H_2SO_4 = 176 g/l
- [MLO] = 3 ml/l [MD] = 8 ml/l
- [Cl^-] = 55 ppm Temp = 22°C
- Flow = 8 lpm RPM: 125

FIG. 48

Without Initiation: IMP seed:



- ◆ SEMATECH Backfilled via, Field 2, 0.29 μm x 1.14 μm , AR = 4.0
- ◆ Bottom Voids - Yes
- ◆ Side wall Voids - No
- ◆ Top Void - No
- ◆ Center Seam - No
- ◆ Film nucleation - poor
- ◆ Void % = 90%
- ◆ 2 second induction

Barrier/Seed Layer

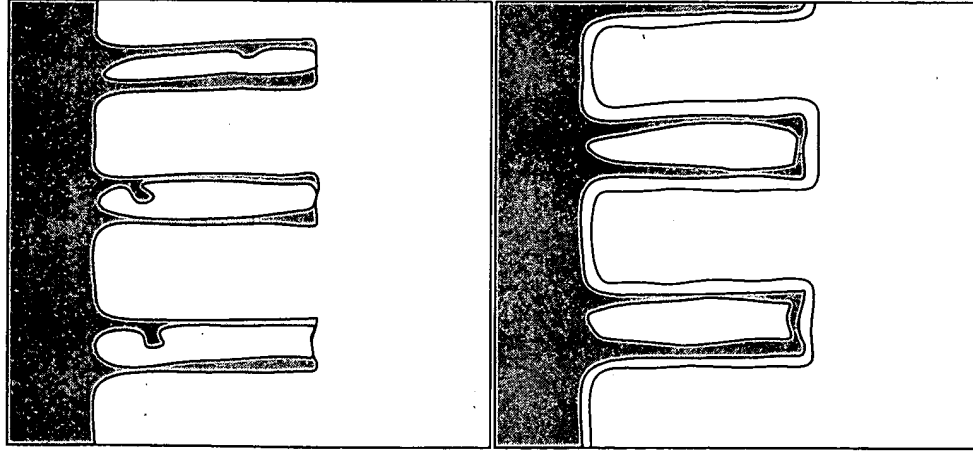
- IMP
- 250Å Ta/1600Å Cu
- Degas Temp.?
- Sputter etch thickness:?
- wafer bias:?

Electroplating

-DC, 7 A
 Bath Conditions
 $[\text{Cu}^{+2}] = 17.3 \text{ g/l}$ $\text{H}_2\text{SO}_4 = 176 \text{ g/l}$
 $[\text{MLiO}] = 3 \text{ ml/l}$ $[\text{MD}] = 8 \text{ ml/l}$
 $[\text{Cl}^-] = 55 \text{ ppm}$ Temp = 22°C
 Flow = 8 lpm RPM: 125

FIG. 49

Without Initiation: IMP seed:



- ◆ SEMATECH Backfilled via, Field 2, 0.29 μm x 1.14 μm , AR = 4.0
- ◆ Bottom Voids - Yes
- ◆ Side wall Voids - No
- ◆ Top Void - No
- ◆ Center Seam - No
- ◆ Film nucleation - poor
- ◆ Void % = 60%
- ◆ 2 second induction

Barrier/Seed Layer

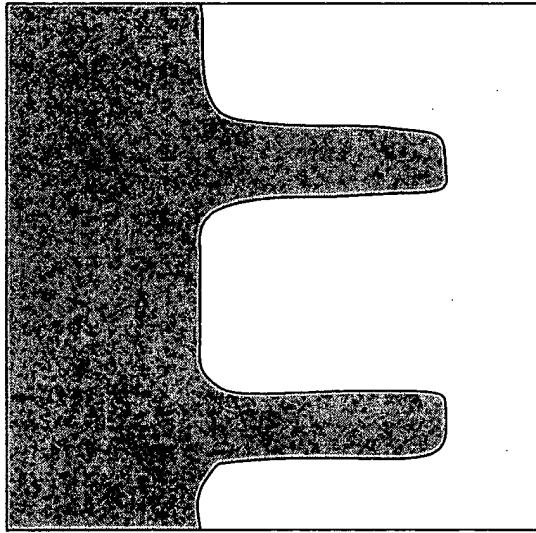
- IMP
- 250Å Ta/2200Å Cu
- Degas Temp.?
- Sputter etch thickness:?
- wafer bias:?

Electroplating

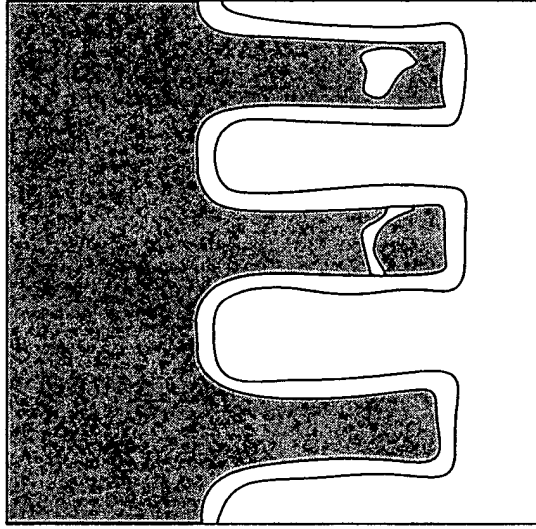
- DC 1 A, 15 sec then 7 A
- Bath Conditions
- [Cu^{+2}] = 17.3 g/l H_2SO_4 = 176 g/l
- [MLO] = 3 ml/l [MD] = 8 ml/l
- [Cl $^-$] = 55 ppm Temp = 22°C
- Flow = 8 lpm RPM: 125

FIG. 50

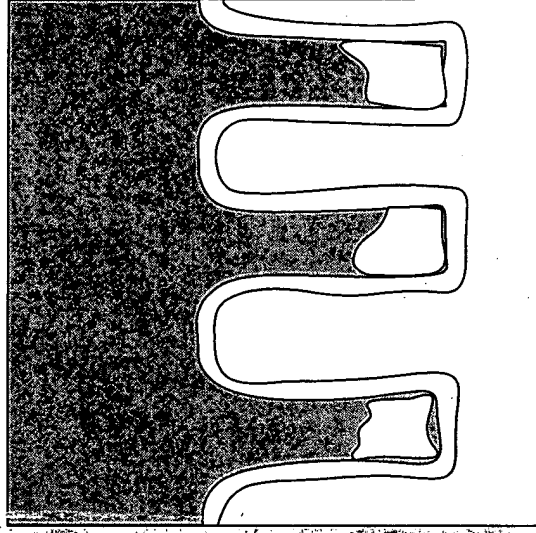
Initiation: Low current, 2 second induction



Field 2, 0.29 μm x 1.14 μm , AR = 4.0



Field 3, 0.24 μm x 1.13 μm , AR = 4.7
• Void % = 1.3%



Field 4, 0.2 μm x 1.0 μm , AR = 5.0
• Void % = 15.8%

- ◆ SEMATECH Backfilled via
- ◆ IMP Seed
- ◆ 250 \AA Ta/1600 \AA Cu

Electroplating

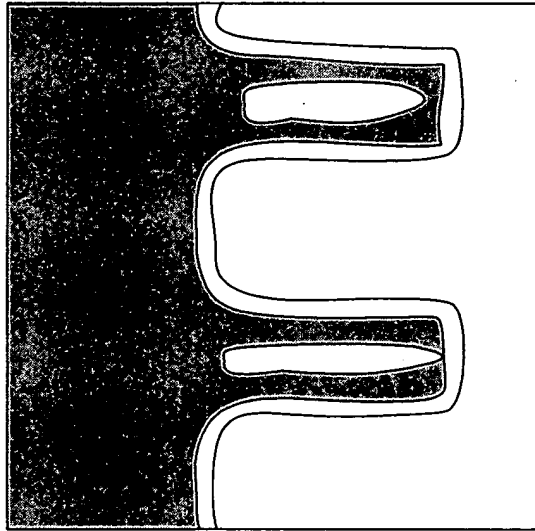
- ◆ Step 1: 1A for 15 sec
- ◆ Step 2: DC, 7 A

Bath Conditions

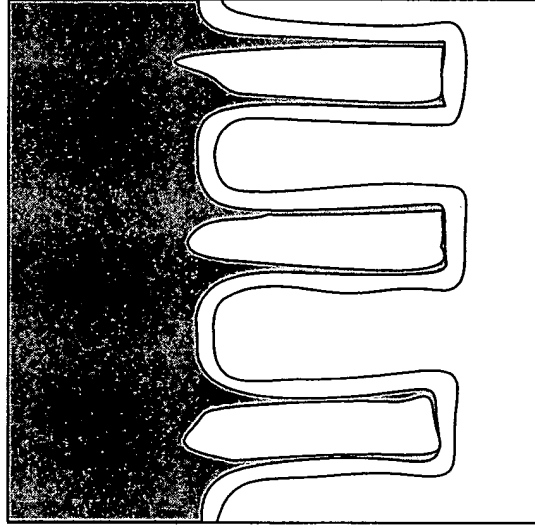
[Cu²⁺] = 17.3 g/l H₂SO₄ = 176 g/l
[MLO] = 3 ml/l [MD] = 8 ml/l
[Cl⁻] = 55 ppm Temp = 22 °C
Flow = 8 lpm RPM: 125

FIG. 51

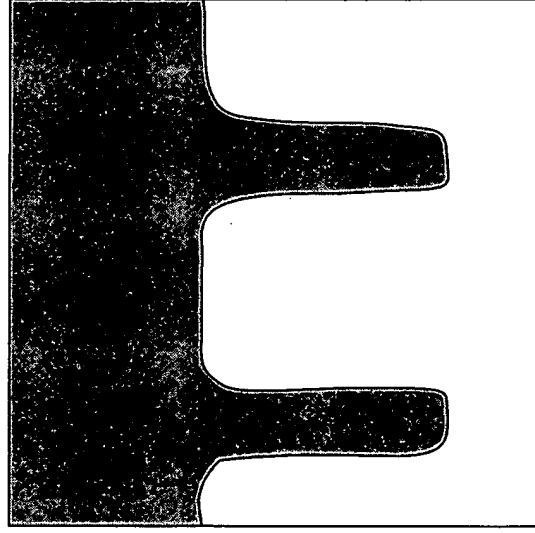
Initiation: Effect of Induction Delay



- ◆ DC, 7 A, 0 sec induction
- ◆ Void % = 16 %



- ◆ DC, 7 A, 2 sec induction
- ◆ Void % = 53 %



- ◆ Step 1: DC 1 A, 15 sec, 2 sec induction
- ◆ Step 2: DC, 7 A
- ◆ Void % = 53 %

◆ SEMATECH Backfilled via

◆ IMP Seed

◆ 250Å Ta/1600Å Cu

Field 2, 0.29 μm x 1.14 μm, AR=4.0

Bath Conditions

[Cu²⁺] = 17.3 g/l H₂SO₄ = 176 g/l
 [MLO] = 3 ml/l [MD] = 8 ml/l
 [Cl⁻] = 55 ppm Temp = 22 °C
 Flow = 8 lpm RPM: 125

FIG. 52

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